

DECLARATION

I, Katsuramaru Fujita, a national of Japan, c/o Sumitomo Chemical Intellectual Property Service, Limited, 5-33, Kitahama 4-chome, Chuo-ku, Osaka 541-8550, Japan, declare that to the best of my knowledge and belief the attached is a full, true, and faithful translation into English made by me of the priority document, Japanese Patent Application No. 2002-86174.

Signed this 11th day of April, 2008

Katsuramaru Fujita

English Translation of JP application No. 2002-086174

[Name of Document] PATENT APPLICATION
[Docket No.] P154188
[Filing Date] March 26, 2002
[Addressee] Commissioner, Patent Office
[International Patent Classification]
H05B 33/14
C07F 15/00
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[Indication on Fees]
[Prepayment Book No.] 010238
[Amount of Payment] 21,000 yen
[List of Articles Filed]
[Name of Article] Specification 1
[Name of Article] Abstract 1
[Number of General Power] 0109029
[Necessity of Proof] Yes

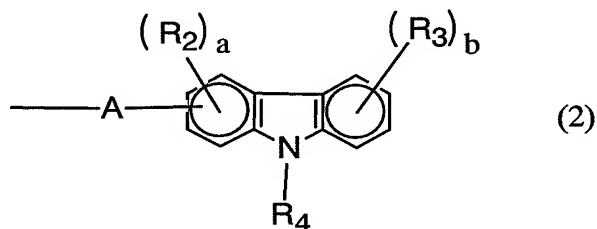
[Name of Document] SPECIFICATION

[Title of the Invention]

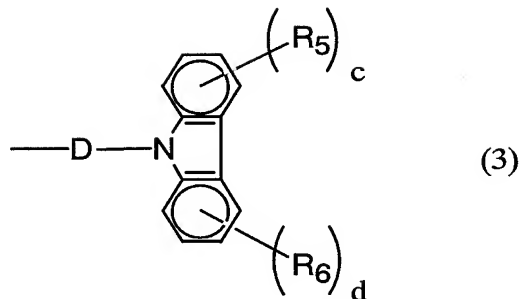
POLYMERIC LIGHT EMITTING SUBSTANCE AND POLYMER LIGHT
EMITTING DEVICE

[Scope of Claims for Patent]

1. A polymeric light emitting substance having a metal complex structure in the main chain or side chain, which shows light emission from triplet excited state, and a monovalent group represented by the following formula (2) or (3),

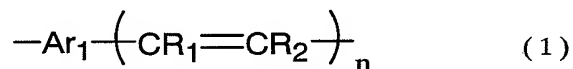


(wherein, A is a conjugated divalent group. R_2 and R_3 each independently represent a halogen atom, alkyl group, alkoxy group, alkylthio group, alkylamino group, alkylsilyl group, aryl group, aryloxy group, arylthio group, arylamino group, arylsilyl group, arylalkyl group, arylalkoxy group, arylalkylthio group, arylalkylamino group, arylalkyl silyl group, acyl group, acyloxy group, imino group, amide group, arylalkenyl group, arylalkynyl group, cyano group, or a monovalent heterocyclic group. R_4 represents alkyl group, aryl group, arylalkyl group, arylalkenyl group, arylalkynyl group, or a monovalent heterocyclic group. a represents an integer of 0 to 3. b represents an integer of 0 to 4. When a or b is two or more, each of R_2 or R_3 may be the same or different, and may be connected mutually to form a ring.)



(wherein, D is a conjugated divalent group. R₅ and R₆ each independently represent a halogen atom, alkyl group, alkoxy group, alkylthio group, alkylamino group, alkylsilyl group, aryl group, aryloxy group, arylthio group, arylamino group, arylsilyl group, arylalkyl group, arylalkoxy group, arylalkylthio group, arylalkyl amino group, arylalkyl silyl group, acyl group, acyloxy group, imino group, amide group, arylalkenyl group, arylalkynyl group, cyano group, or a monovalent heterocyclic group. c and d each independently represent an integer of 0 to 4. When c or d is two or more, each of R₅ or R₆ may be the same or different, and may be connected mutually to form a ring.)

2. A polymeric light emitting substance according to claim 1, wherein said polymeric light emitting substance comprises a repeating unit represented by the following formula (1),



(wherein, Ar₁ represents an arylene group or a divalent heterocyclic group. R₁ and R₂ each independently represent a hydrogen atom, alkyl group, aryl group, monovalent heterocyclic group, a group represented by the above formula (2), a group represented by the above formula (3), or cyano group. n is 0 or 1.).

3. A polymer light emitting device comprising at least a light emitting layer which contains the polymeric compound according to claim 1 or 2 between electrodes consisting of an anode and a cathode.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a polymeric light emitting substance complex, and a light-emitting device using said polymeric light emitting substance (hereinafter, may be referred to as polymer LED) as a light-emitting substance.

[0002]

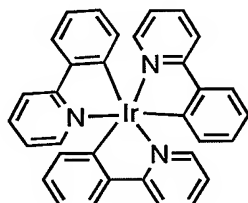
[Prior Art]

As a light-emitting material used for a light emitting layer of light-emitting device, devices using a metal complex (hereafter may be referred to as triplet light-emitting complex) showing light emission from triplet excited state have been known.

[0003]

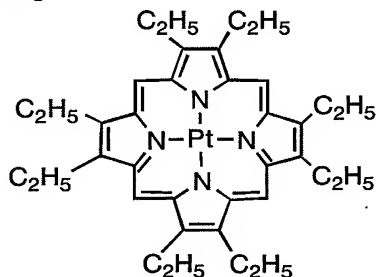
As the triplet light-emitting complex, for example, Ir(ppy)₃ which includes iridium as the central metal, (Appl.Phys.Lett., 75, 4(1999)), PtOEP which includes platinum as the central metal (Nature, 395, 151(1998)), Eu(TTA)₃phen which includes europium as the central metal (Jpn. J. Appl. Phys., 34, 1883(1995)) are known.

[0004]



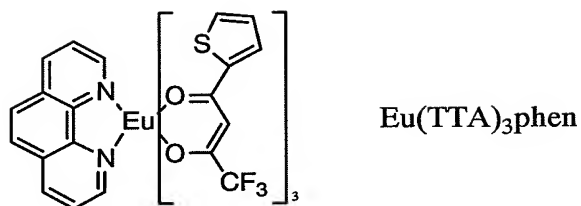
Ir(ppy)₃

[0005]



PtOEP

[0006]



[0007]

[Problems to be Solved by the Invention]

However, for forming a light emitting layer using the above well-known triplet light-emitting complexes, only the methods, such as vacuum-depositing method, are applicable, and it has been difficult to form a light emitting layer by coating method.

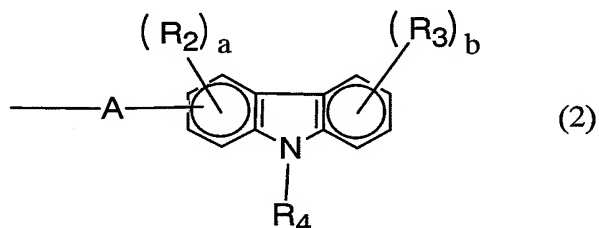
[0008]

The object of the present invention is to provide a new polymeric light emitting substance having a metal complex structure in the molecule, which can form a light emitting layer by coating method, and a light emitting device using said polymeric light emitting substance.

[0009]

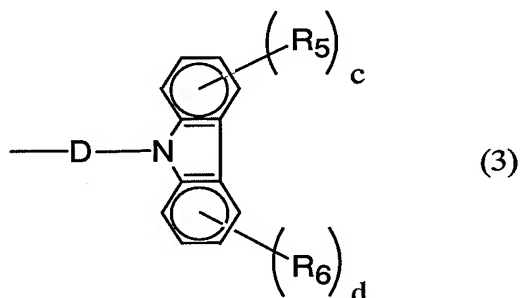
[Means for Solving the Problem]

As the result of the intensive studies, the present inventors found that a polymeric light emitting substance having a group represented by the following formula (2) or (3) in the main chain or side chain, has a triplet light emitting complex structure in the molecule, and can form a light emitting layer by coating method, and completed the present invention.



(in formula (2), A is a conjugated divalent group. R₂ and R₃ each independently represent a halogen atom, alkyl group, alkoxy group, alkylthio group, alkylamino group, alkylsilyl group, aryl group, aryloxy group, arylthio group, arylamino

group, arylsilyl group, arylalkyl group, arylalkoxy group, arylalkylthio group, arylalkylamino group, arylalkyl silyl group, acyl group, acyloxy group, imino group, amide group, arylalkenyl group, arylalkynyl group, cyano group, or a monovalent heterocyclic group. R_4 represents alkyl group, aryl group, arylalkyl group, arylalkenyl group, arylalkynyl group, or a monovalent heterocyclic group. a represents an integer of 0 to 3. b represents an integer of 0 to 4. When a or b is two or more, each of R_2 or R_3 may be the same or different, and may be connected mutually to form a ring.)



(in formula (3), D is a conjugated divalent group. R_5 and R_6 each independently represent a halogen atom, alkyl group, alkoxy group, alkylthio group, alkylamino group, alkylsilyl group, aryl group, aryloxy group, arylthio group, arylamino group, arylsilyl group, arylalkyl group, arylalkoxy group, arylalkylthio group, arylalkyl amino group, arylalkyl silyl group, acyl group, acyloxy group, imino group, amide group, arylalkenyl group, arylalkynyl group, cyano group, or a monovalent heterocyclic group. c and d each independently represent an integer of 0 to 4. When c or d is two or more, each of R_5 or R_6 may be the same or different, and may be connected mutually to form a ring.)

[0010]

[Mode for Carrying out the Invention]

In the present invention, the metal complex structure showing light emission from triplet excited state means a structure derived from a triplet light-emitting complex.

The triplet light-emitting complex which is a ground material of the metal complex structure showing light emission

from triplet excited state will be explained.

The triplet light-emitting complex is usually a heavy metal complex, for example, a complex which may generate phosphorescence emission from said complex. Complexes in which fluorescence emission is observed in addition to phosphorescence emission are also included.

[0011]

The triplet light-emitting complexes are those having been used as a low molecular weight EL material. Such materials are disclosed, for example, in: Nature, (1998) 395,151; Appl. Phys. Lett.,(1999) 75(1), 4; Proc. SPIE-Int. Soc. Opt. Eng.,(2001) 4105 ; (Organic Light-Emitting Materials and Devices IV),119; J. Am. Chem. Soc., (2001) 123, 4304; Appl. Phys. Lett.,(1997) 71(18), 2596; Syn. Met.,(1998) 94(1),103; Syn. Met.,(1999) 99(2), 1361; and Adv. Mater.,(1999),11 (10),852.

[0012]

The central metal of the metal complex structure showing light emission from triplet excited state of the present invention is usually an atom having atomic number of 50 or more, spin-orbit interaction occurs in the complex, and intersystem crossing between a singlet state and a triplet state can occur in the metal.

[0013]

As the central metal, exemplified are rhenium, iridium, osmium, scandium, yttrium, platinum, gold; and lanthanoids such as europium, terbium, thulium, dysprosium, samarium, praseodymium, gadolinium, etc. Iridium, platinum, gold, and europium are preferable; iridium, platinum, and gold are especially preferable; and iridium is the most preferable.

[0014]

The ligand of the triplet light-emitting complex is usually an organic ligand, and the number of carbon atoms is usually about 3 to 60.

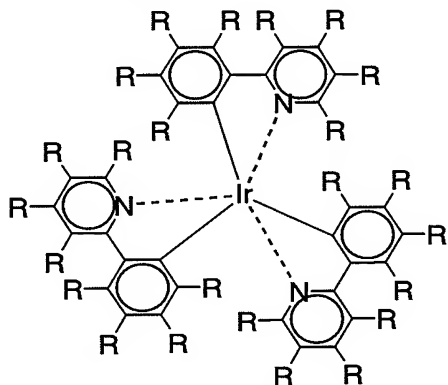
[0015]

As the ligand of the triplet light-emitting complex, exemplified are 8-quinolinol and derivatives thereof,

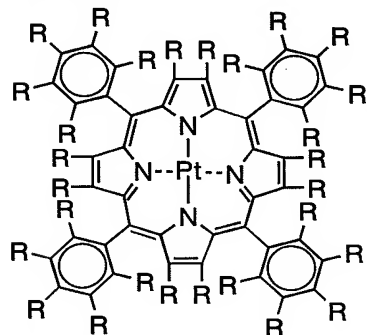
benzoquinolinol and derivatives thereof, 2-phenyl-pyridine and derivatives thereof, 2-phenyl-benzothiazole and derivatives thereof, 2-phenyl-benzoxazole and derivatives thereof, porphyrin derivatives thereof, etc.

[0016]

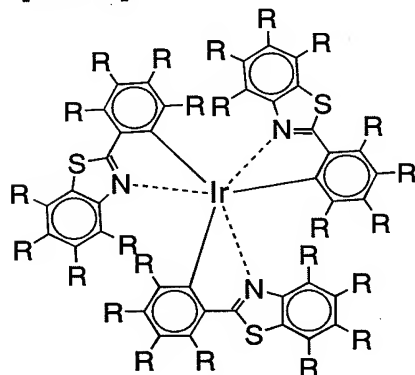
As the triplet light-emitting complex, followings are exemplified.

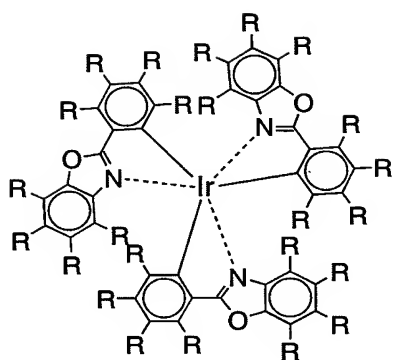


[0017]

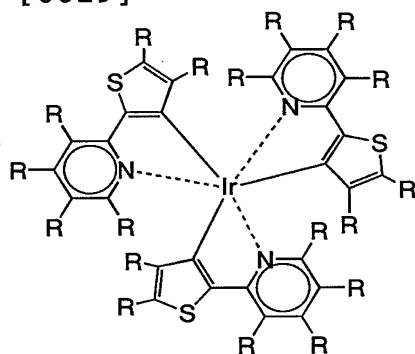


[0018]

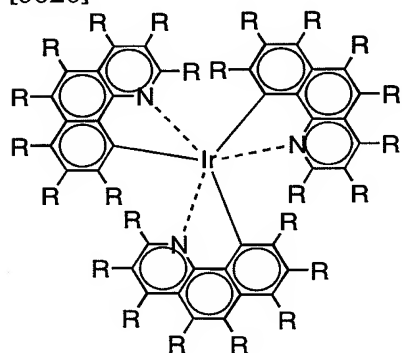




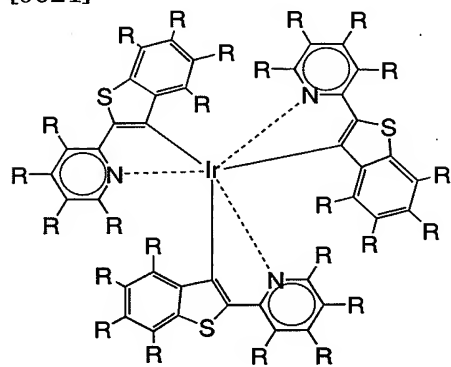
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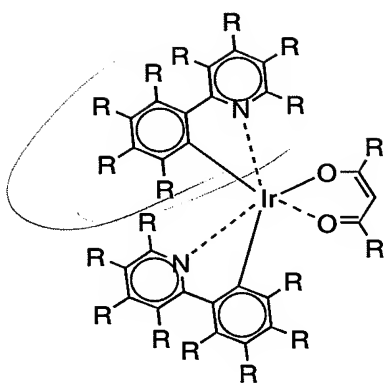
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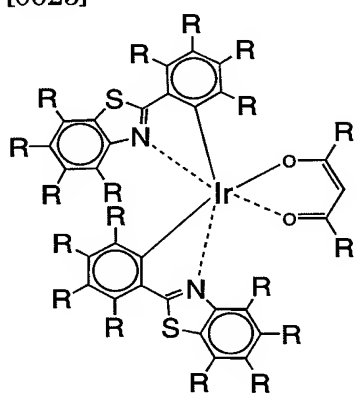
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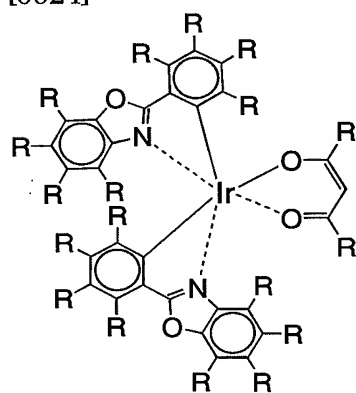
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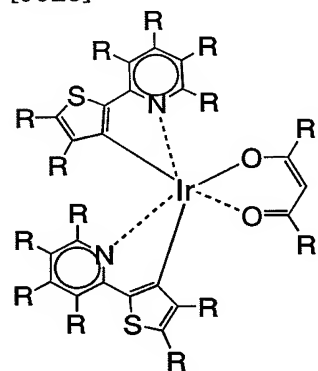
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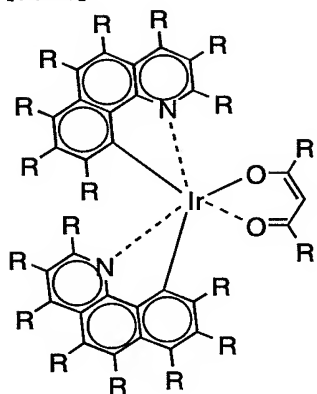
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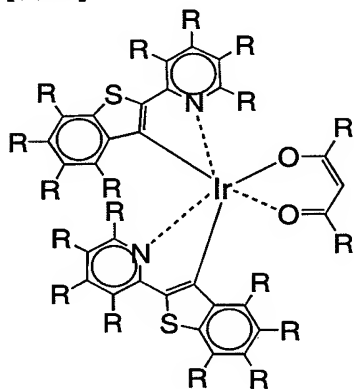
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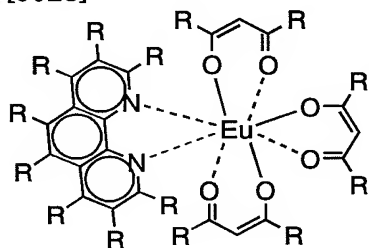
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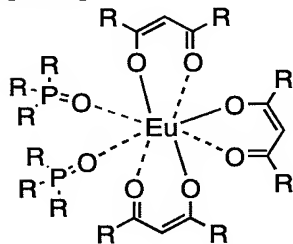
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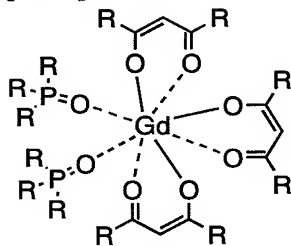
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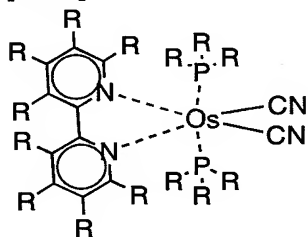
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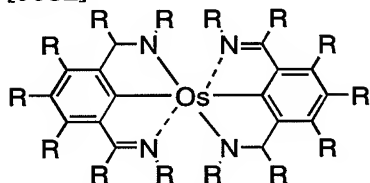
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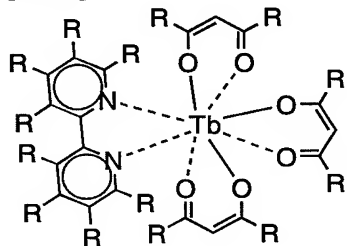
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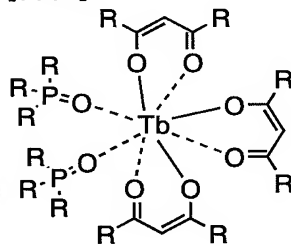
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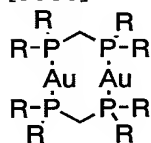
[0033]



[0034]



[0035]



[0036]

Here, R each independently represent a group selected from a hydrogen atom, alkyl group, alkoxy group, alkylthio group, alkyl silyl group, alkylamino group, aryl group, aryloxy group, arylalkenyl group, arylalkynyl group, arylamino group, monovalent heterocyclic group, a group represented by the above formula (2), a group represented by the above formula (3), and cyano group. In order to improve the solubility into a solvent, it is preferable that, and the form of repeating groups has little symmetry.

[0037]

The alkyl group may be any of linear, branched or cyclic. The number of carbon atoms is usually from about 1 to 20, and specific examples thereof include methyl group, ethyl group, propyl group, i-propyl group, butyl group, i-butyl group, t-butyl group, pentyl group, hexyl group, cyclohexyl group, heptyl group, octyl group, 2-ethylhexyl group, nonyl group, decyl group, 3,7-dimethyloctyl group, lauryl group, etc.; and pentyl group, hexyl group, octyl group, 2-ethylhexyl group, decyl group, and 3,7-dimethyloctyl group are preferable.

[0038]

The alkoxy group may be any of linear, branched or cyclic. The number of carbon atoms is usually from about 1 to 20, and specific examples thereof include methoxy group, ethoxy group, propyloxy group, i-propyloxy group, butoxy group, i-butoxy group, t-butoxy group, pentyloxy group, hexyloxy group, cyclohexyloxy group, heptyloxy group, octyloxy group, 2-ethyl hexyloxy group, nonyloxy group, decyloxy group, 3,7-dimethyl octyloxy group, lauryloxy group, etc.; and pentyloxy group, hexyloxy group, octyloxy group, 2-ethylhexyloxy group, decyloxy group, and 3,7-dimethyloctyloxy group are preferable.

[0039]

The alkylthio group may be any of linear, branched or cyclic. The number of carbon atoms is usually from about 1 to 20, and specific examples thereof include methylthio group, ethylthio group, propylthio group, i-propylthio group, butylthio group,

i-butylthio group, t-butylthio group, pentylthio group, hexylthio group, cyclohexylthio group, heptylthio group, octylthio group, 2-ethylhexylthio group, nonylthio group, decylthio group, 3,7-dimethyloctylthio group, laurylthio group, etc.; and pentylthio group, hexylthio group, octylthio group, 2-ethylhexylthio group, decylthio group, and 3,7-dimethyloctylthio group are preferable.

[0040]

The alkylsilyl group may be any of linear, branched or cyclic, and the number of carbon atoms is usually from about 1 to 60. Specific examples thereof include methylsilyl group, ethylsilyl group, propylsilyl group, i-propylsilyl group, butylsilyl group, i-butylsilyl group, t-butylsilyl group, pentylsilyl group, hexylsilyl group, cyclohexylsilyl group, heptylsilyl group, octylsilyl group, 2-ethylhexylsilyl group, nonylsilyl group, decylsilyl group, 3,7-dimethyloctyl silyl group, laulylsilyl group, trimethylsilyl group, ethyldimethyl silyl group, propyldimethylsilyl group, i-propyldimethylsilyl group, butyldimethylsilyl group, t-butyldimethylsilyl group, pentyldimethylsilyl group, hexyldimethylsilyl group, heptyldimethylsilyl group, octyldimethylsilyl group, 2-ethylhexyl-dimethylsilyl group, nonyldimethylsilyl group, decyldimethylsilyl group, 3,7-dimethyloctyl-dimethyl silyl group, lauryldimethylsilyl group, etc.; and pentylsilyl group, hexylsilyl group, octylsilyl group, 2-ethylhexylsilyl group, nonylsilyl group, decylsilyl group, 3,7-dimethyloctyl silyl group, pentyldimethylsilyl group, hexyldimethylsilyl group, octyldimethylsilyl group, 2-ethylhexyl-dimethylsilyl group, decyldimethylsilyl group, and 3,7-dimethyloctyl-dimethyl silyl group are preferable.

[0041]

The alkylamino group may be any of linear, branched or cyclic, and may be monoalkylamino group or dialkylamino group. The number of carbon atoms is usually from about 1 to 40, and specific examples thereof include methylamino group, dimethyl

amino group, ethylamino group, diethylamino group, propyl amino group, i-propylamino group, butylamino group, i-butylamino group, t-butylamino group, pentylamino group, hexylamino group, cyclohexylamino group, heptylamino group, octylamino group, 2-ethylhexylamino group, nonylamino group, decylamino group, 3,7-dimethyloctylamino group, laurylamino group, etc.; and pentylamino group, hexylamino group, octylamino group, 2-ethylhexylamino group, decylamino group, and 3,7-dimethyl octylamino group are preferable.

[0042]

The aryl group has usually about 6 to 60 atoms. Specific examples thereof include phenyl group, C₁-C₁₂ alkoxyphenyl group (C₁-C₁₂ represents the number of carbon atoms 1-12. Hereafter the same.), C₁-C₁₂ alkylphenyl group, 1-naphtyl group, 2-naphtyl group, etc.; and C₁-C₁₂ alkoxyphenyl group, and C₁-C₁₂ alkylphenyl group are preferable.

[0043]

The aryloxy group has usually about 6 to 60. Specific examples thereof include phenoxy group, C₁-C₁₂ alkoxyphenoxy group, C₁-C₁₂ alkylphenoxy group, 1-naphtyloxy group, 2-naphtyloxy group, etc.; and C₁-C₁₂ alkoxyphenoxy group, and C₁-C₁₂ alkylphenoxy group are preferable.

[0044]

The arylalkyl group has usually about 7 to 60 atoms. Specific examples thereof include phenyl-C₁-C₁₂ alkyl group, C₁-C₁₂ alkoxyphenyl-C₁-C₁₂ alkyl group, C₁-C₁₂ alkylphenyl-C₁-C₁₂ alkyl group, 1-naphtyl-C₁-C₁₂ alkyl group, 2-naphtyl-C₁-C₁₂ alkyl group, etc.; and C₁-C₁₂ alkoxyphenyl-C₁-C₁₂ alkyl group, and C₁-C₁₂ alkyl phenyl-C₁-C₁₂ alkyl group are preferable.

[0045]

The arylalkoxy group has usually about 7 to 60 atoms. Specific examples thereof include phenyl-C₁-C₁₂ alkoxy group, C₁-C₁₂ alkoxyphenyl-C₁-C₁₂ alkoxy group, C₁-C₁₂ alkyl phenyl-C₁-C₁₂ alkoxy group, 1-naphtyl-C₁-C₁₂ alkoxy group, 2-naphtyl-C₁-C₁₂ alkoxy group, etc.; and C₁-C₁₂ alkoxy phenyl-C₁-C₁₂ alkoxy group, and C₁-C₁₂ alkyl phenyl-C₁-C₁₂ alkoxy

group are preferable.

[0046]

The arylalkenyl group has usually about 8 to 60 carbon atoms. Specific examples thereof include cis-phenylalkenyl group, trans-phenylalkenyl group, cis-tolylalkenyl group, cis-1-naphtylalkenyl group, trans-1-naphtylalkenyl group, cis-2-naphtylalkenyl group, trans-2-naphtylalkenyl group, etc.

[0047]

The arylalkynyl group has usually about 8 to 60 carbon atoms. Specific examples thereof include phenylalkynyl group, tolylalkynyl group, 1-naphtylalkynyl group, 2-naphtylalkynyl group, etc.

[0048]

The arylamino group has usually about 6 to 60 atoms. Specific examples thereof include phenylamino group, diphenylamino group, C₁-C₁₂ alkoxyphenylamino group, di(C₁-C₁₂ alkoxyphenyl) amino group, di(C₁-C₁₂ alkylphenyl) amino group, 1-naphtylamino group, 2-naphtylamino group, etc.; and C₁-C₁₂ alkylphenylamino group and di(C₁-C₁₂ alkylphenyl) amino group are preferable.

[0049]

The monovalent heterocyclic group means an atomic group in which a hydrogen atom is removed from a heterocyclic compound, and usually has about 4 to 60 carbon atoms. Specific examples thereof include thienyl group, C₁-C₁₂ alkylthienyl group, pyroryl group, furyl group, pyridyl group, C₁-C₁₂ alkylpyridyl group, etc.; and thienyl group, C₁-C₁₂ alkylthienyl group, pyridyl group, and C₁-C₁₂ alkylpyridyl group, are preferable.

[0050]

Among the examples of R, in order to improve the solubility of a light emitting polymer in a solvent, it is preferable that one or more of them contains a cyclic or long alkyl chain, and exemplified are: cyclopentyl group, cyclohexyl group, pentyl group, hexyl group, octyl group, 2-ethylhexyl group, decyl group, and 3,7-dimethyloctyl group. Moreover, two

substituents may be connected to form a ring. Furthermore, a carbon atom of a part of the alkyl chain may be replaced by a group containing a hetero atom, and examples of the hetero atoms include an oxygen atom, a sulfur atom, a nitrogen atom, etc.

[0051]

Furthermore, as for the aryl group and the monovalent heterocyclic group in R, they may have one or more substituents.

[0052]

The polymeric light emitting substance of the present invention may have a metal complex structure showing light emission from triplet excited state in the main chain, in the side chain, or at the terminal of the main chain.

[0053]

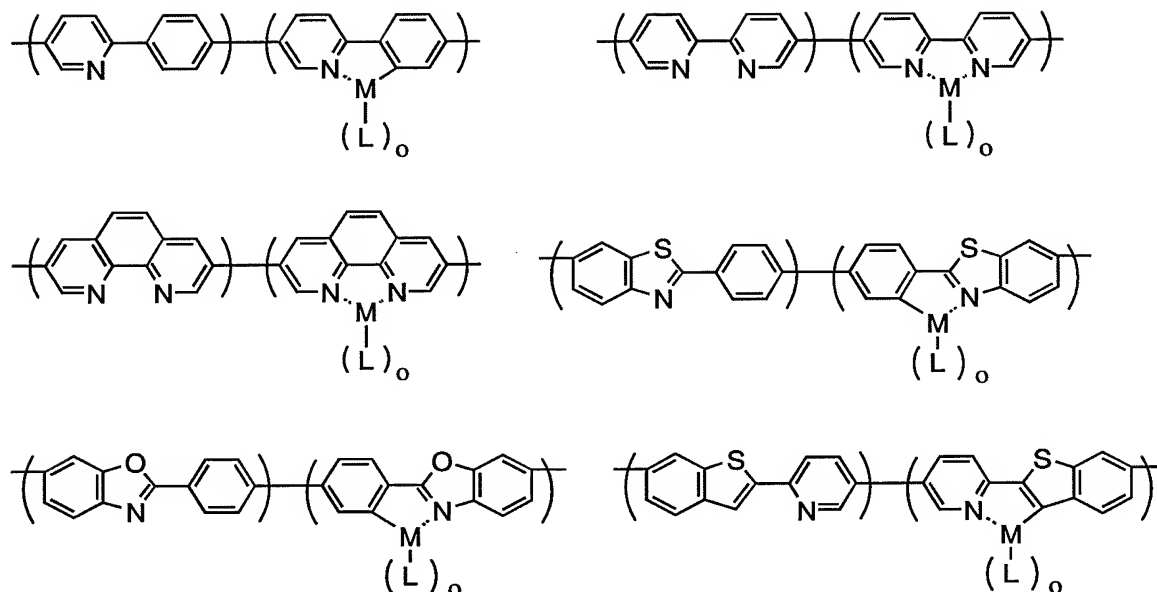
The polymeric light emitting substance having a metal complex structure showing light emission from triplet excited state in the main chain means the case wherein an aromatic ring part or condensed ring part which coordinate to the complex showing light emission from triplet excited state is contained in the main chain, or the case wherein a metal is contained in the main chain.

[0054]

Moreover, when at least one of the ligands contained in the metal complex structure of the light emitting polymer of the present invention includes the same structure with the repeating unit contained in the polymer main chain, it is preferable as the metal content can be controlled.

That is, when the structure of the ligand is contained in the main chain, the light emitting polymer of the present invention can be manufactured by performing complex-formation after manufacturing a polymer compound. Specifically, the following structure are exemplified.

[0055]



[0056]

The polymeric light emitting substance having a metal complex structure showing light emission from triplet excited state in the side chain means the case wherein an aromatic ring part or condensed ring part which coordinate to the complex showing light emission from triplet excited state is connected to the main chain through bonding. Here, the bond means a direct bond such as a direct bond and a double bond; a bond through an atom, such as oxygen atom, sulfur atom, and selenium atom; or a bond through a divalent-bond such as a methylene group, alkylene group, and arylene group, etc.

Among them, it is preferable that a metal complex structure showing light emission from triplet excited state is contained in a side chain having conjugated bonding.

[0057]

When a metal complex structure showing light emission from triplet excited state is contained in a side chain, it is preferable that an aromatic ring contained in at least one ligand of said metal complex structure and an aromatic ring contained in the polymer main chain are connected through a carbon-carbon single bond.

[0058]

Of the polymeric light-emitting substance of the present invention, it is preferable that the main chain is a conjugated type polymeric light-emitting substance. Here, the conjugated type polymeric light-emitting substance means a polymeric light-emitting substance in which delocalized π electron pair exist along with the main-chain of the polymer, i.e., a polymeric light-emitting substance whose main chain is a conjugated polymer. As this delocalized electron, a unpaired electron or a lone electron pair may join to the resonance instead of a double bond.

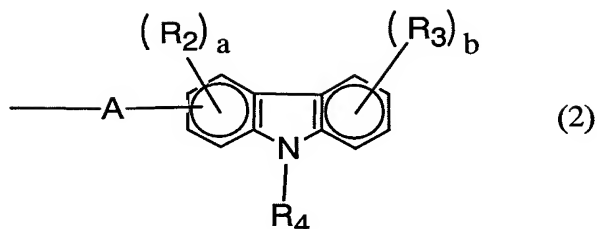
[0059]

One embodiment of the present invention is a polymeric light-emitting substance having two or more kinds of metal complex structures showing light emission from triplet excited state, i.e., a polymeric light-emitting substance having 2 or more kinds of metal complex structures showing light emission from triplet excited state, on two or more of the main chain, side chain, or the terminal. Metal complex structures may have the same metal each other, and may have different metals. Moreover, metal complex structures may have mutually different light emission color. For example, exemplified is a case where both of a metal complex structure which emits green light and a metal complex structure which emits red light are contained in one polymeric light-emitting substance. The case is preferable, since a light emission color is controllable by designing to contain an appropriate amount of the metal complex structure.

[0060]

The metal complex of the present invention has a monovalent group represented by the below formula (2) or (3). Thereby, light emitting efficiency can be improved.

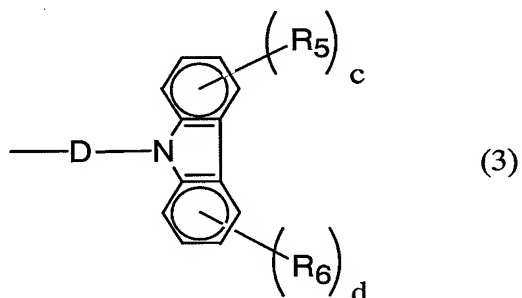
[0061]



[0062]

In the formula, A is a conjugated divalent group. R₂ and R₃ each independently represent a halogen atom, alkyl group, alkoxy group, alkylthio group, alkylamino group, alkylsilyl group, aryl group, aryloxy group, arylthio group, arylamino group, arylsilyl group, arylalkyl group, arylalkoxy group, arylalkylthio group, arylalkylamino group, arylalkyl silyl group, acyl group, acyloxy group, imino group, amide group, arylalkenyl group, arylalkynyl group, cyano group, or a monovalent heterocyclic group. R₄ represents alkyl group, aryl group, arylalkyl group, arylalkenyl group, arylalkynyl group, or a monovalent heterocyclic group. a represents an integer of 0 to 3. b represents an integer of 0 to 4. When a or b is two or more, each of R₂ or R₃ may be the same or different, and may be connected mutually to form a ring.

[0063]



[0064]

In the formula, D is a conjugated divalent group. R₅ and R₆ each independently represent a halogen atom, alkyl group, alkoxy group, alkylthio group, alkylamino group, alkylsilyl group, aryl group, aryloxy group, arylthio group, arylamino group, arylsilyl group, arylalkyl group, arylalkoxy group, arylalkylthio group, arylalkyl amino group, arylalkyl silyl

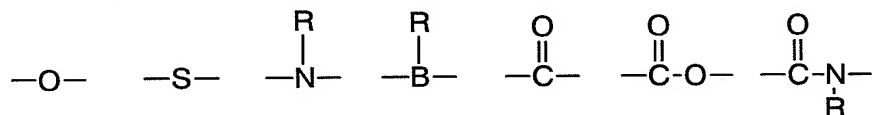
group, acyl group, acyloxy group, imino group, amide group, arylalkenyl group, arylalkynyl group, cyano group, or a monovalent heterocyclic group. c and d each independently represent an integer of 0 to 4. When c or d is two or more, each of R₅ or R₆ may be the same or different, and may be connected mutually to form a ring.

[0065]

In R₂ to R₆, the halogen atom, alkyl group, alkoxy group, alkylthio group, alkylamino group, alkylsilyl group, aryl group, aryloxy group, arylthio group, arylamino group, arylsilyl group, arylalkyl group, arylalkoxy group, arylalkylthio group, arylalkylamino group, arylalkylsilyl group, acyl group, acyloxy group, imino group, amide group, arylalkenyl group, arylalkynyl group, cyano group, and monovalent heterocyclic group, are the same as those of R exemplified above.

[0066]

As the conjugated divalent group in A or D, exemplified are vinylene group, acetylene group, an arylene group, a divalent heterocyclic group, bonding units shown below, and two or more combination thereof.



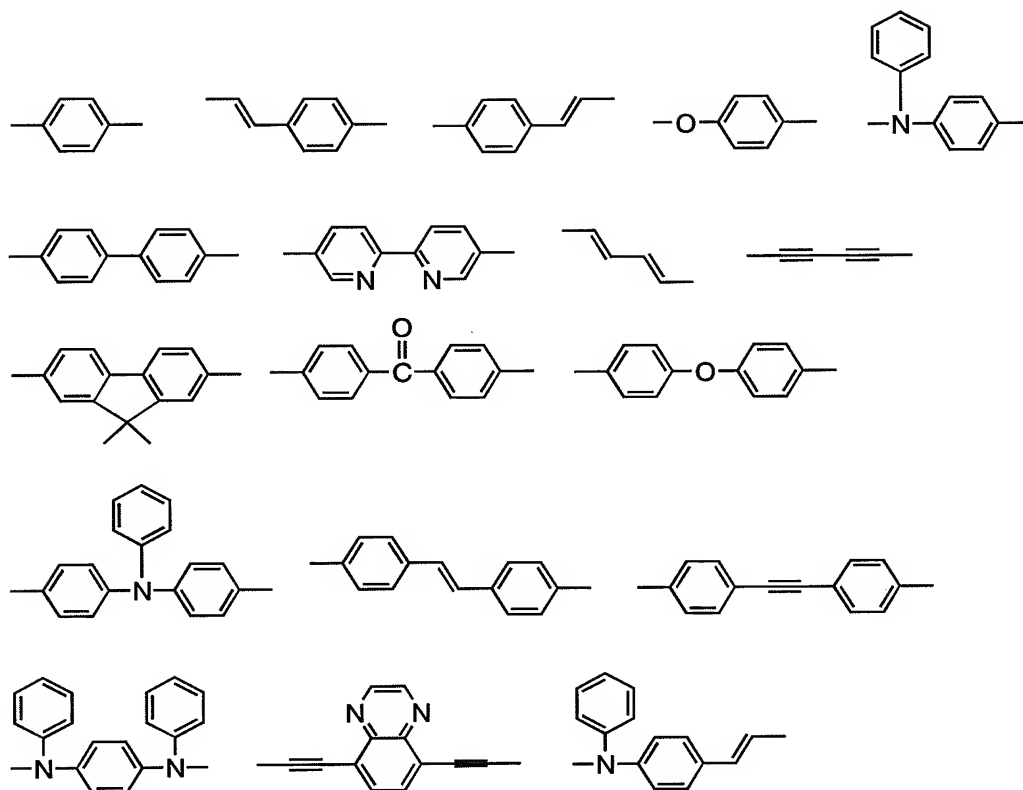
(In the formula, R represents alkyl group, aryl group, or a monovalent heterocyclic group.)

[0067]

As the arylene group and the divalent heterocyclic group in A or D, they are the same as those exemplified below.

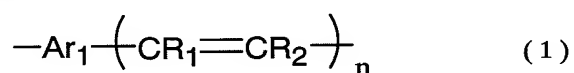
[0068]

As the concrete examples of A or D, following groups are exemplified, without being limited thereto.



[0069]

As for the light emitting polymer of the present invention, it is preferable that the repeating unit shown by the below formula (1) is contained.



In the formula, Ar_1 represents an arylene group or a divalent heterocyclic group. R_1 and R_2 each independently represent a hydrogen atom, alkyl group, aryl group, monovalent heterocyclic group, a group shown by the above formula (2), a group shown by the above formula (3), or cyano group. n is 0 or 1.

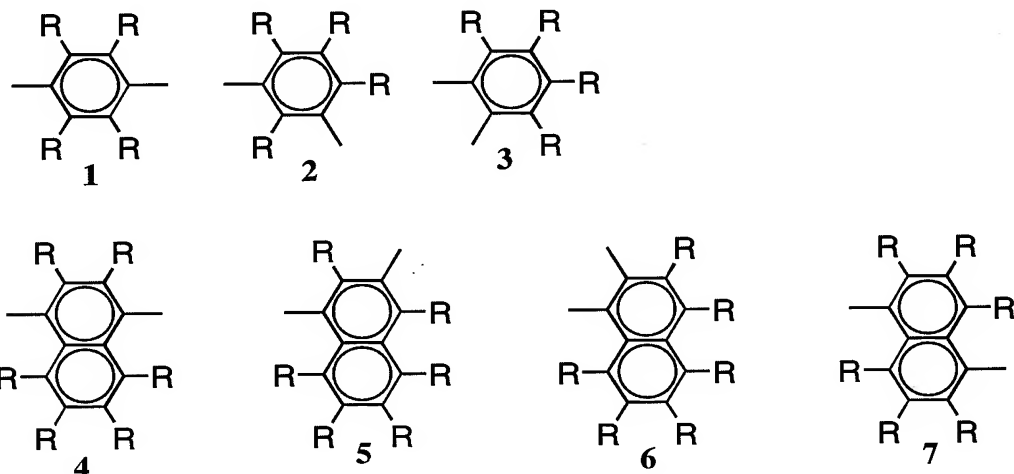
[0070]

Examples of the alkyl group, aryl group, and monovalent heterocyclic group shown by R_1 or R_2 , they are the same as those exemplified as the above-mentioned R.

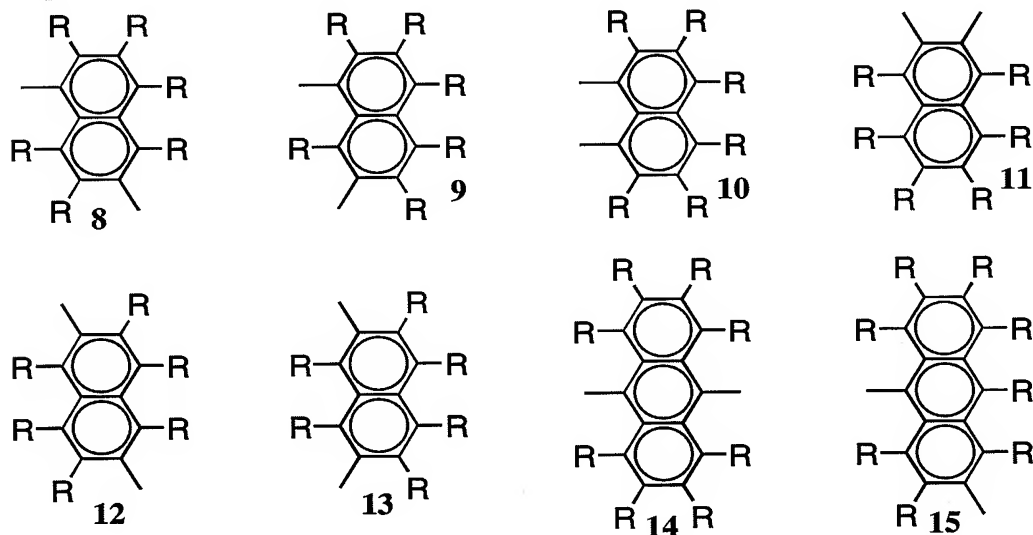
[0071]

The arylene group represented by Ar_1 has usually 6-60, preferably 6-20 carbon atoms, and examples thereof include phenylene group (for example, following formulas 1-3), naphthalenediyl group (following formulas 4-13), anthracenylene group (following formulas 14-19), biphenylene group (following formulas 20-25), triphenylene group (following formulas 26-28), condensed-ring compound group (following formulas 29-38), etc. Here, the number of carbon atoms of substituent R is not counted as the number of carbon atoms of arylene group.

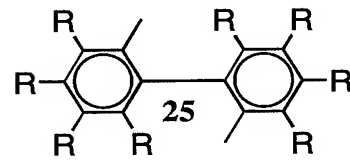
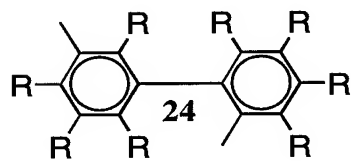
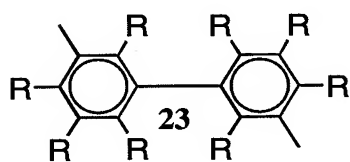
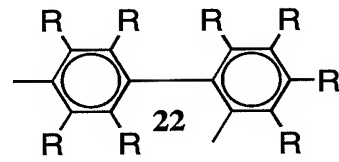
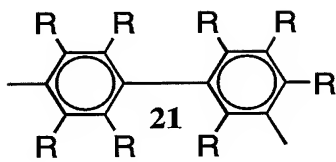
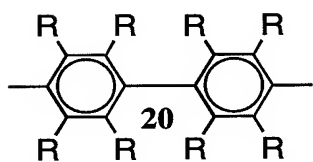
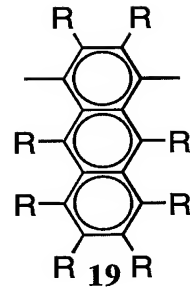
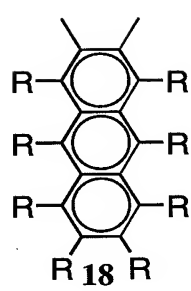
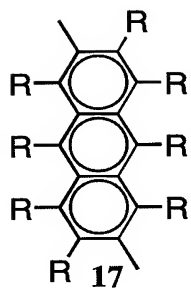
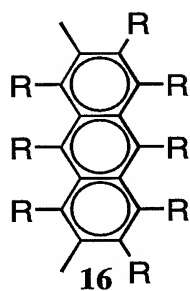
[0072]



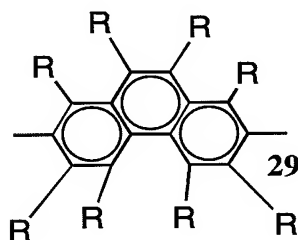
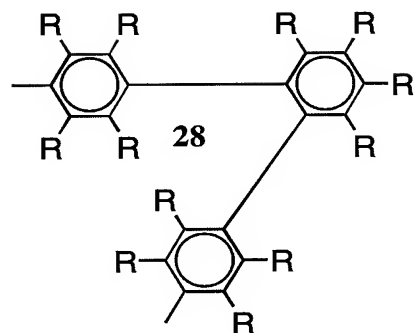
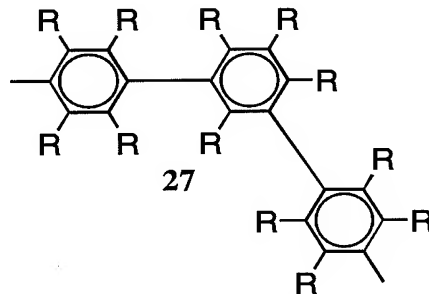
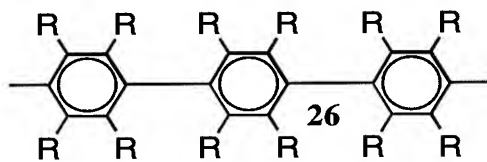
[0073]



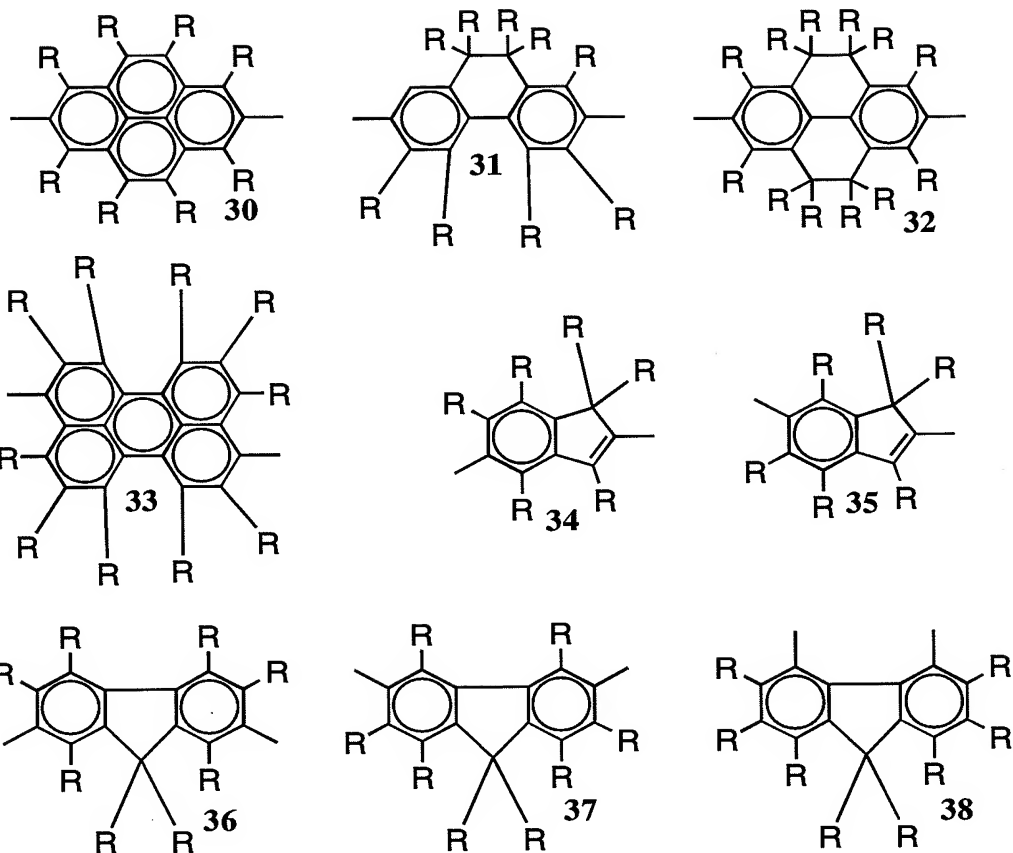
[0074]



[0075]



[0076]



[0077]

In the present invention, the divalent heterocyclic group means an atomic group in which two hydrogen atoms are removed from a heterocyclic compound, and the number of carbon atoms is usually 4-60, and preferably 4-20. Here, the number of carbon atoms of substituent is not counted as the number of carbon atoms of the divalent heterocyclic group.

[0078]

The heterocyclic compound means an organic compound having a cyclic structure in which at least one heteroatom such as oxygen, sulfur, nitrogen, phosphorus, boron, etc. is contained in the cyclic structure as the element other than carbon atoms.

[0079]

Examples of the divalent heterocyclic group include followings.

[0080]

Divalent heterocyclic groups containing nitrogen as a hetero atom; pyridine-diyl group (following formulas 39-44), diaza phenylene group (following formulas 45-48), quinolinediyl group (following formulas 49-63), quinoxalinediyl group (following formulas 64-68), acridinediyl group (following formulas 69-72), bipyridyldiyl group (following formulas 73-75), phenanthrolinediyl group (following formulas 76-78), etc.

Groups having a fluorene structure containing silicon, nitrogen, sulfur, selenium, etc. as a hetero atom (following formulas 79-93). It is preferable to have an aromatic amine monomer containing a nitrogen atom, such as carbazole of formulas 82-84 or triphenylaminediyl group, in view of light emitting efficiency.

[0081]

5 membered heterocyclic groups containing silicon, nitrogen, sulfur, selenium, etc. as a hetero atom: (following formulas 94-98).

[0082]

Condensed 5 membered heterocyclic groups containing silicon, nitrogen, sulfur, selenium, etc. as a hetero atom: (following formulas 99-109), benzothiadiazole-4,7-diyl group, benzo oxadiazole-4,7-diyl group, etc.

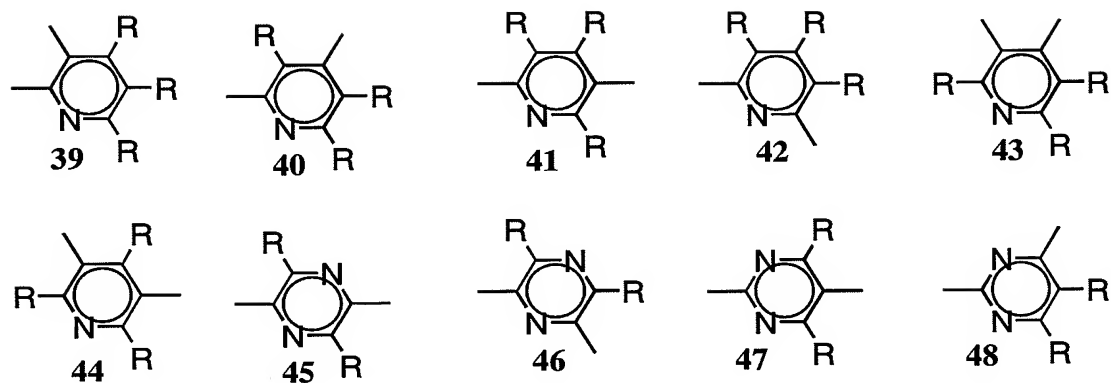
[0083]

5 membered heterocyclic groups containing silicon, nitrogen, sulfur, selenium, etc. as a hetero atom, which are connected at the a position of the hetero atom to form a dimer or an oligomer (following formulas 110-118); and

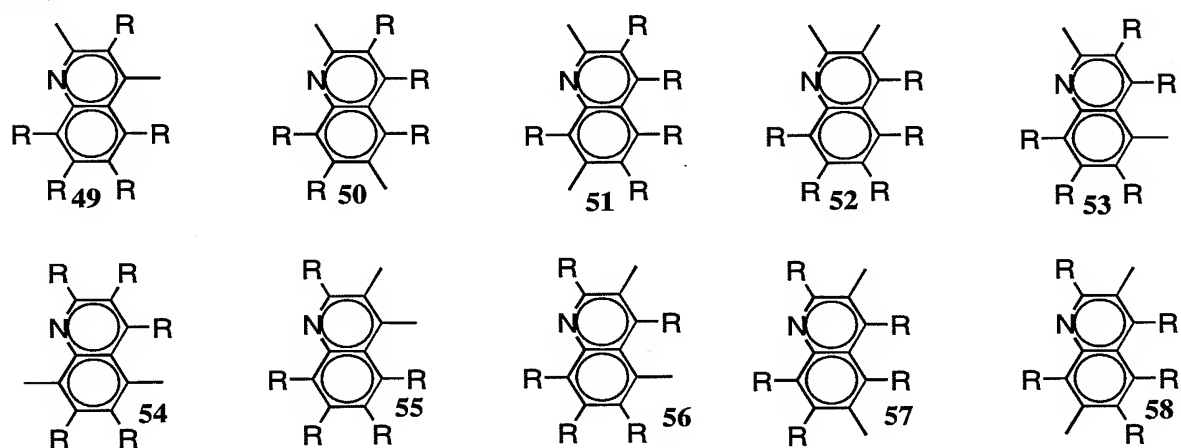
[0084]

5 membered ring heterocyclic groups containing silicon, nitrogen, oxygen, sulfur, selenium, as a hetero atom is connected with a phenyl group at the a position of the hetero atom (following formulas 112-118).

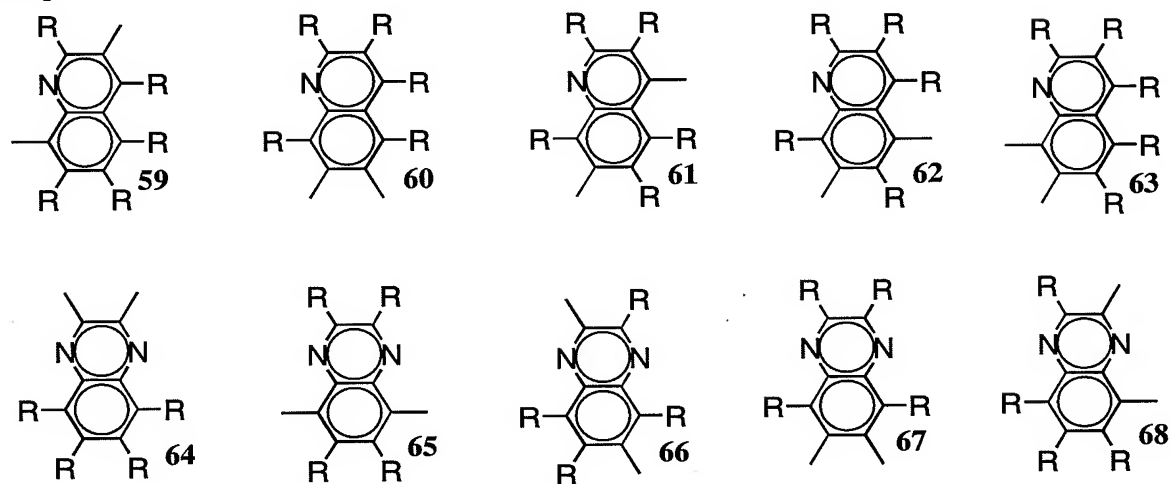
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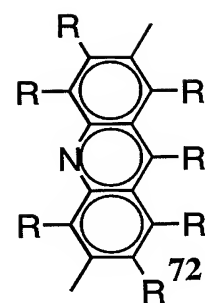
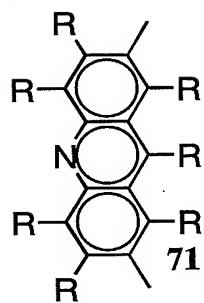
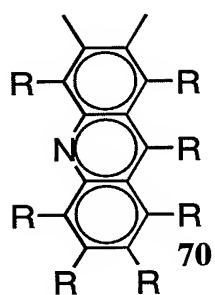
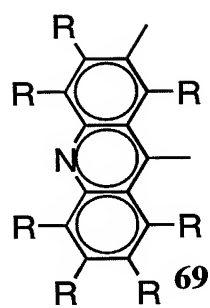
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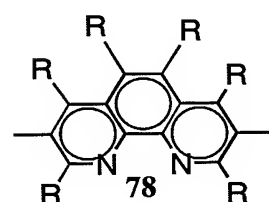
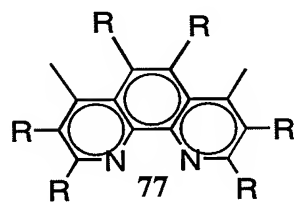
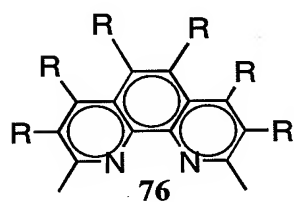
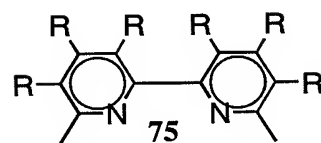
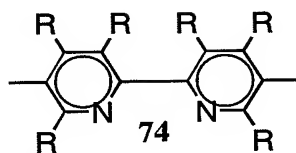
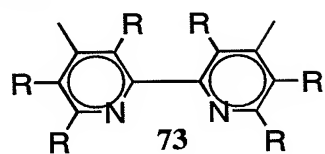
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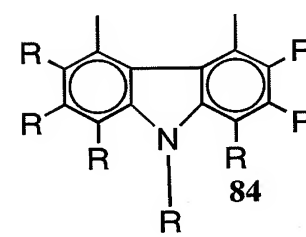
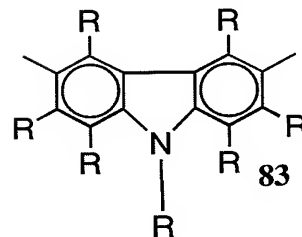
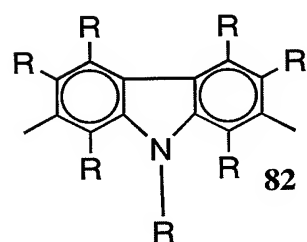
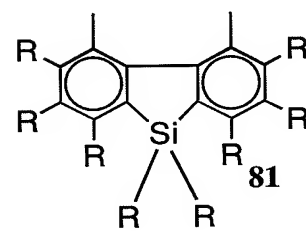
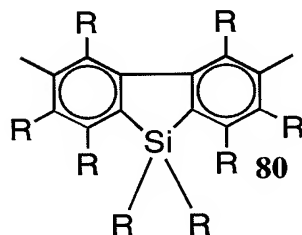
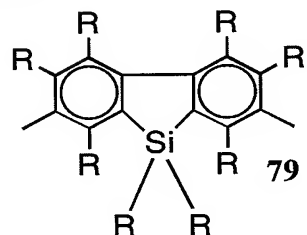
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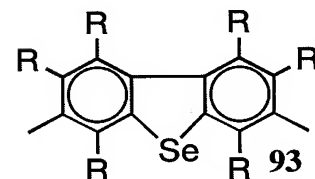
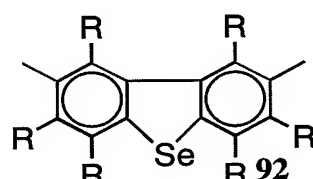
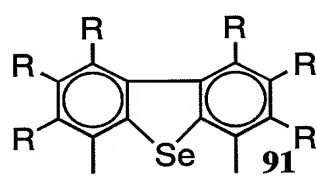
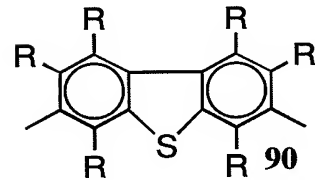
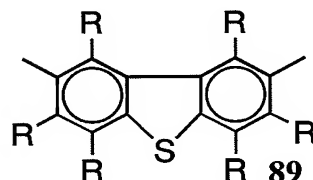
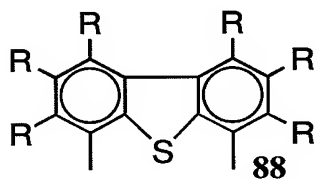
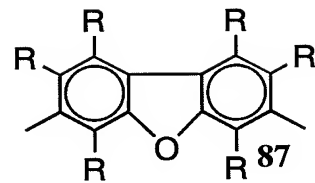
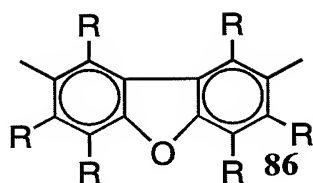
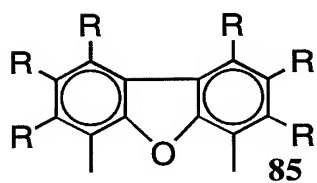
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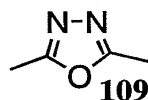
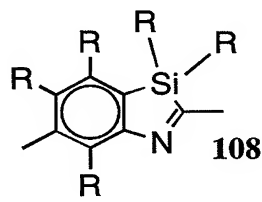
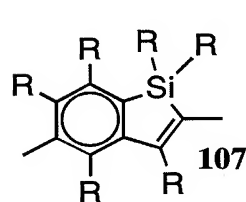
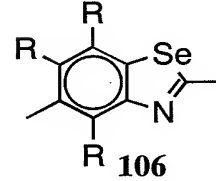
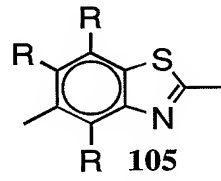
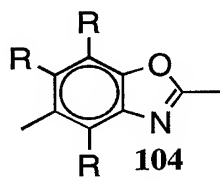
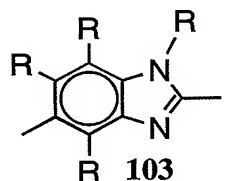
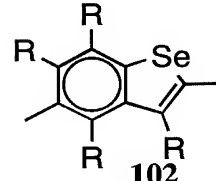
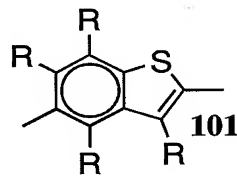
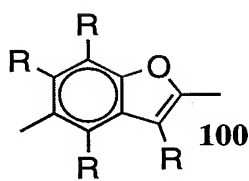
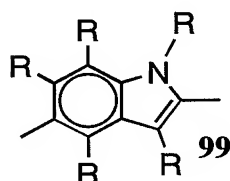
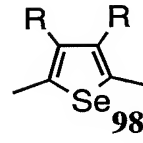
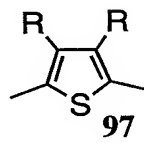
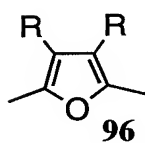
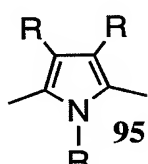
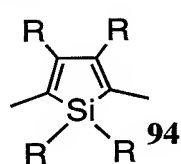
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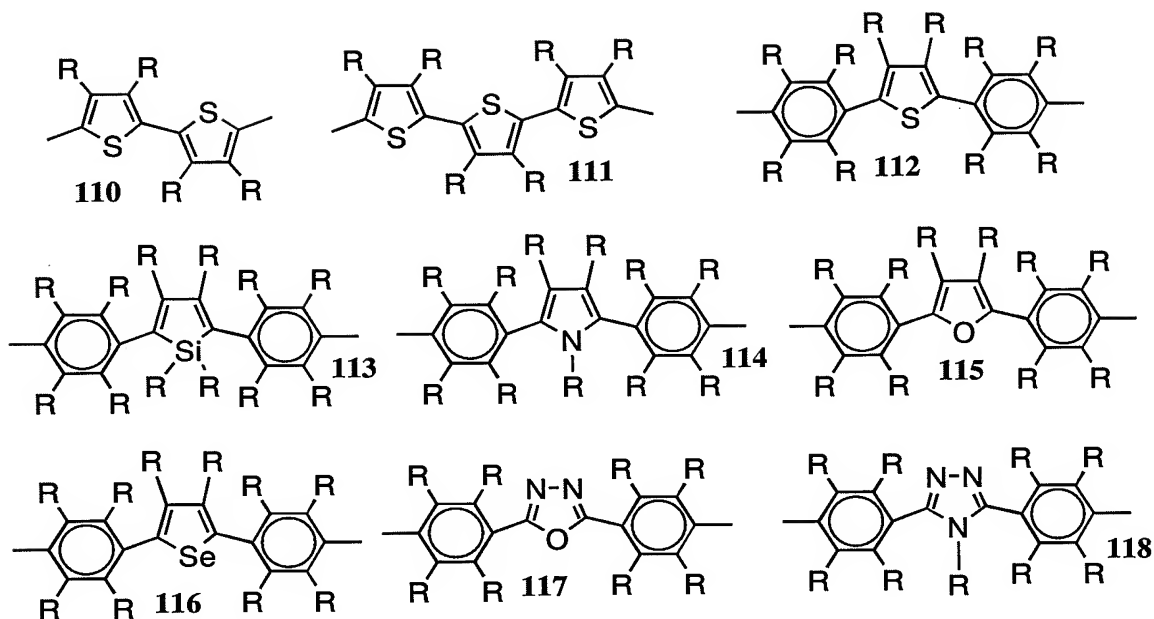
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[0092]



[0093]

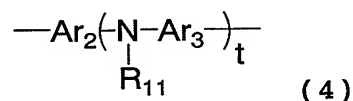


[0094]

Here, R is the same group as those described above.

[0095]

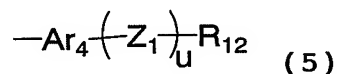
As for the polymeric light-emitting substance of the present invention, it is preferable that the repeating unit represented by the below formula (4) is included in respect of light emitting efficiency.



[0096]

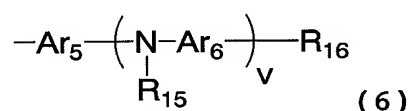
In the formula, Ar₂ and Ar₃ each independently represent an arylene group or a divalent heterocyclic group. Ar₂ and Ar₃ are not connected. R₁₁ represents alkyl group, aryl group, monovalent heterocyclic group, a group represented by the above formula (2), a group represented by the above formula (3), a group represented by the following formula (5), or a group represented by the following formula (6). t is an integer of 1-4.

[0097]



In the formula, Ar₄ is an arylene group or a divalent heterocyclic group. R₁₂ is a hydrogen atom, alkyl group, aryl group, monovalent heterocyclic group, or a group represented by the below formula (6). Z₁ represents -CR₁₃=CR₁₄- or -C≡C-. R₁₃ and R₁₄ each independently represent a hydrogen atom, alkyl group, aryl group, a monovalent heterocyclic group, a group represented by the above formula (2), a group represented by the above formula (3), or cyano group. u is an integer of 0-2.

[0098]



In the formula, Ar₅ and Ar₆ each independently represent an arylene group or a divalent heterocyclic group. R₁₅ represents an alkyl group, aryl group, a group represented by the above formula (2), a group represented by the above formula (3), or a monovalent heterocyclic group. R₁₆ represents a hydrogen atom, alkyl group, aryl group, or monovalent heterocyclic group. v is an integer of 1-4.

[0099]

As the arylene group and divalent heterocyclic group in Ar₂ to Ar₆, exemplified are the same as those of the above Ar₁.

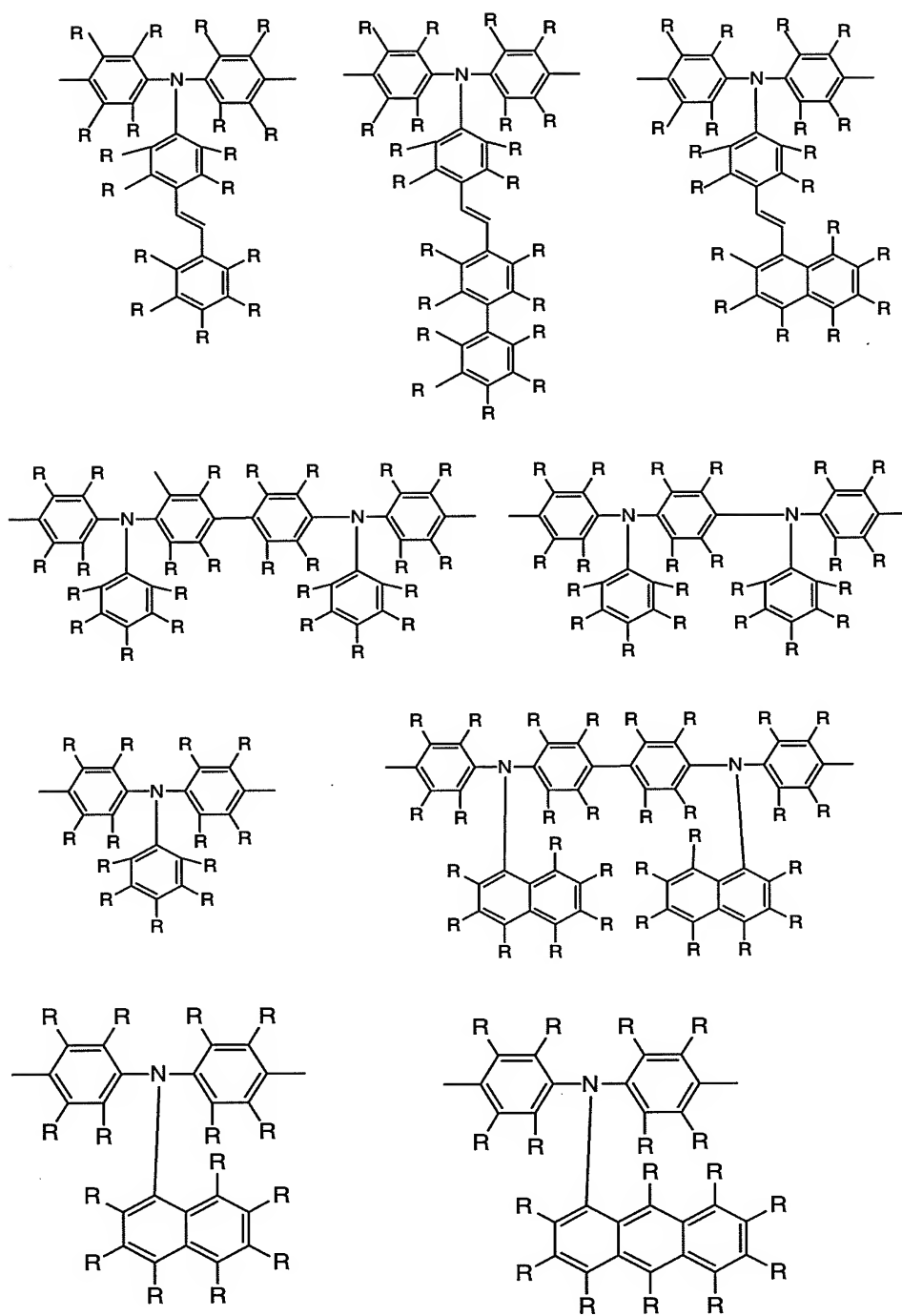
[0100]

As the alkyl group, aryl group and monovalent heterocyclic group in R₁₁ to R₁₆, exemplified are the same as those of the above R.

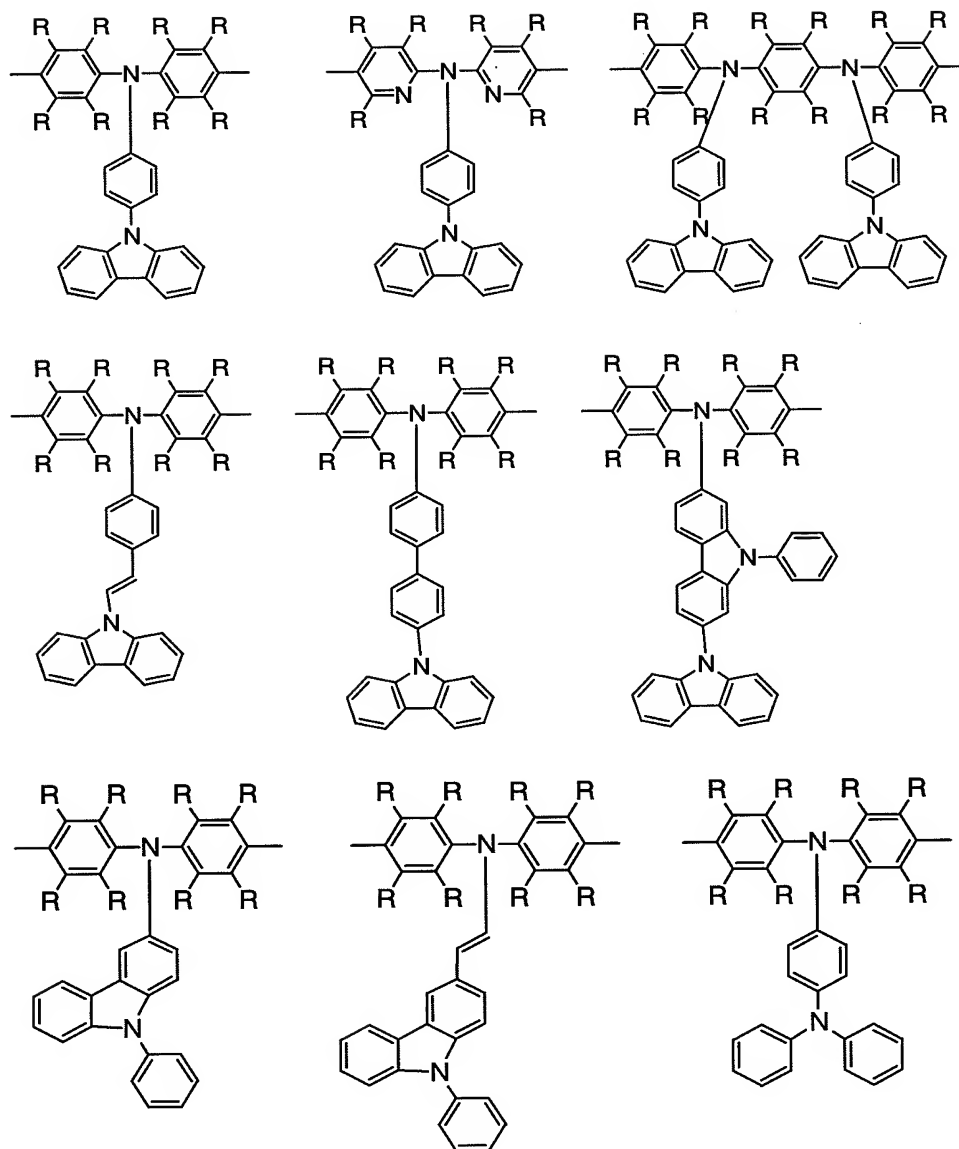
[0101]

As the preferable example of the repeating unit represented by the above formula (21), exemplified are those represented by the following formulae.

[0102]



[0103]



In the formula, R is the same as that of the above.

[0104]

Furthermore, the end group of polymeric compound may also be protected with a stable group since if a polymerization active group remains intact, there is a possibility of reduction in light emitting property and life-time when made into an device. Those having a conjugated bond continuing to a conjugated structure of the main chain are preferable, and there are exemplified structures connected to an aryl group

or heterocyclic compound group via a carbon-carbon bond. Specifically, substituents shown by Chemical Formula 10 in JP-A-9-45478 are exemplified.

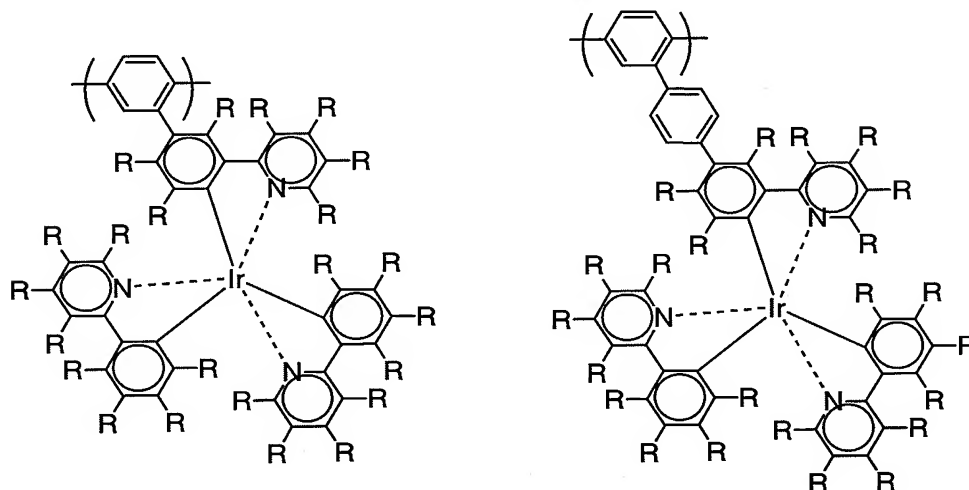
[0105]

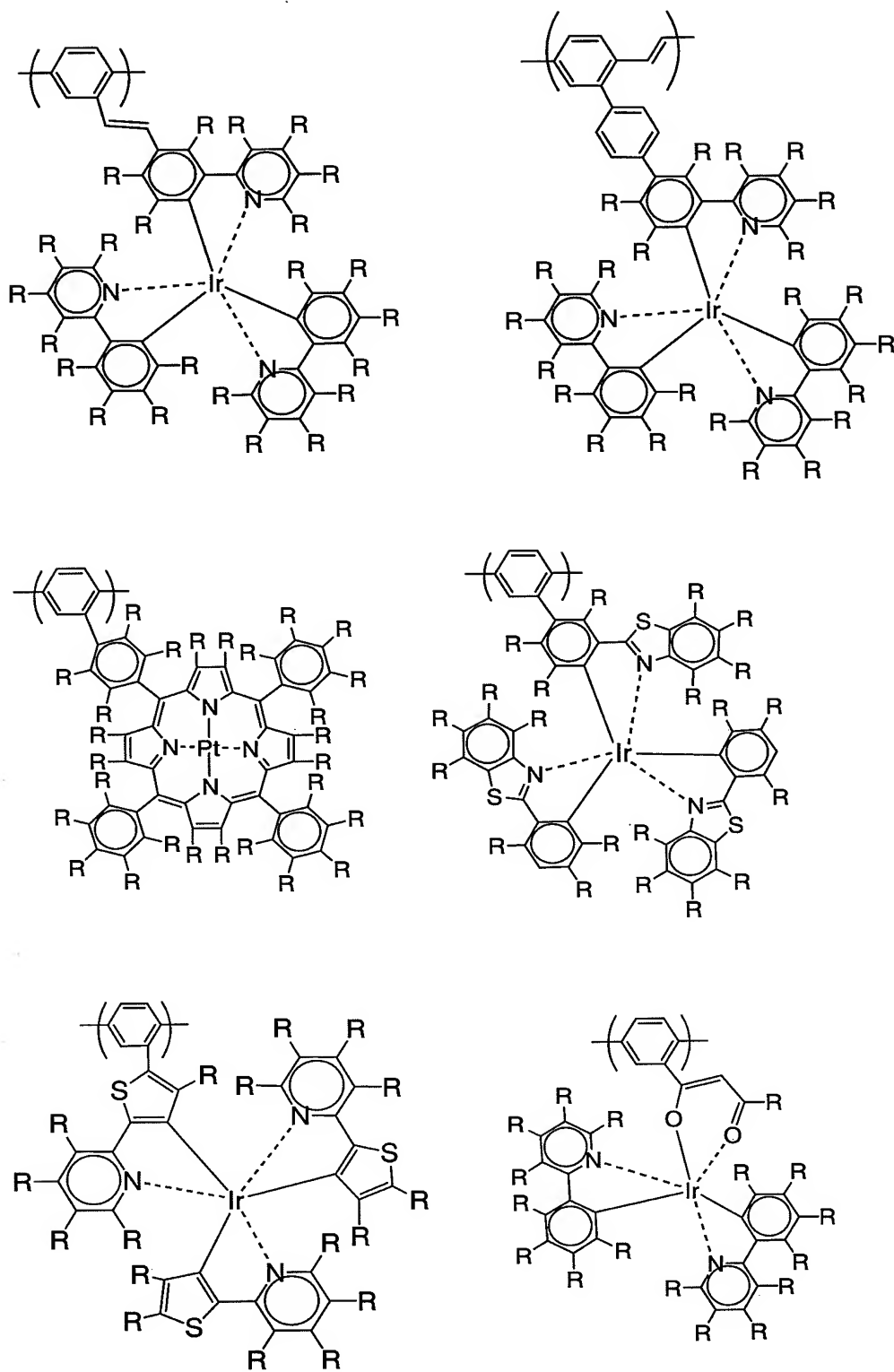
The polymer of the present invention may also be a random, block or graft copolymer, or a polymer having an intermediate structure thereof, for example, a random copolymer having block property. From the viewpoint for obtaining a polymeric fluorescent substance having high fluorescent quantum yield, random copolymers having block property and block or graft copolymers are more preferable than complete random copolymers. Further, a polymer having a branched main chain and more than three terminals, and a dendrimer may also be included.

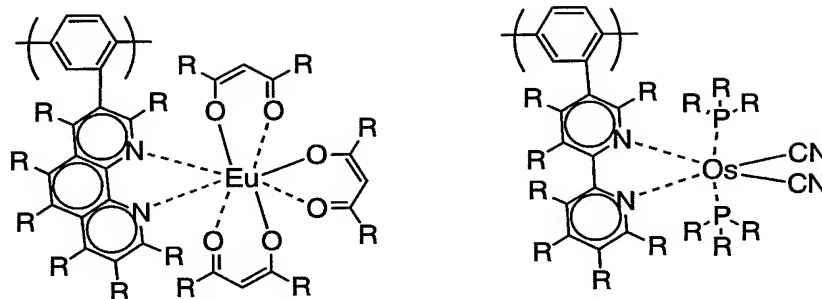
[0106]

The polymeric light emitting substance of the present invention preferably contains 0.01 to 10 mole% of the repeating unit having a complex structure showing light emission from triplet excited state.

Here, as the complex structure showing light emission from triplet excited state, exemplified are: molecular groups in which two or more of Rs are removed of the triplet light emitting complex shown above; and structures shown below.







[0107]

Next, the manufacture method of the light emitting polymer of the present invention is explained.

As for the case where the light emitting polymer of the present invention has vinylene group in the main chain, a method described in JP-A-5-202355 is exemplified. That is, exemplified are: polymerization by Wittig reaction of a compound having a formyl group and a compound having phosphonium methyl group, or a compound having a formyl group and a phosphonium methyl group; polymerization by Heck reaction of a compound having a vinyl group and a compound having a halogen atom; polycondensation by dehydrohalogenation method of a compound having two or more monohalogenated methyl groups; polycondensation by sulfonium-salt decomposition method of a compound having two or more sulfonium methyl group; polymerization by Knoevenagel reaction of a compound having formyl group and a compound having cyano group; and polymerization by McMurry reaction of a compound having two or more formyl group.

When the light emitting polymer of the present invention has a triple bond in the main chain, Heck reaction for example can be used.

[0108]

When there contained neither vinylene group nor triple bond in the main chain, exemplified are: a polymerization method by Suzuki coupling reaction from the corresponding monomers; a polymerization method by Grignard reaction; a polymerization method by Ni(0) catalyst; a polymerization method by an

oxidizer, such as FeCl_3 ; an electrochemically oxidation polymerization; and a method by decomposition of an intermediate polymer having a suitable elimination group.

[0109]

Among these, a polymerization by Wittig reaction, a polymerization by Heck reaction, a polymerization by Knoevenagel reaction, polymerization method by Suzuki coupling reaction, a polymerization by Grignard reaction, a polymerization by $\text{Ni}(0)$ catalyst are preferable, since it is easy to carry out structure control.

[0110]

Specifically, a compound having a plurality of reactive substituents is dissolved in an organic solvent, according to necessity, and can be reacted using alkali or appropriate catalyst, at the temperature between the boiling point and the melting point of the organic solvent of the organic solvent.

Known methods which can be used are described in: Organic Reactions, Volume 14, page 270-490, John Wiley & Sons, Inc., 1965 ; Organic Reactions, Volume 27, page 345-390, John Wiley & Sons, Inc., 1982; Organic Syntheses, Collective Volume VI, page 407-411, John Wiley & Sons, Inc., 1988; Chemical Review (Chem.Rev.), Volume 95, page 2457 (1995); Journal of Organometallic Chemistry (J.Organomet.Chem.), Volume 576, page 147 (1999); Journal of Praktical Chemistry (J.Prakt.Chem.), Volume 336, page 247 (1994); and Macromolecular Chemistry, Macromolecular Symposium (Makromol. Chem., Macromol.Symp.), Volume 12th, page 229 (1987).

[0111]

It is preferable that the organic solvent used is subjected to a deoxygenation treatment sufficiently and the reaction is progressed under an inert atmosphere, generally for suppressing a side reaction, though the treatment differs depending on compounds and reactions used. Further, it is preferable to conduct a dehydration treatment likewise. However, this is not applicable in the case of a reaction in a two-phase system with water, such as a Suzuki coupling reaction.

[0112]

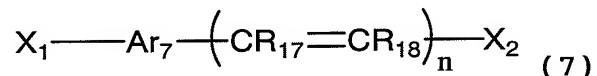
For the reaction, alkali and a suitable catalyst is added. They can be selected according to the reaction to be used. It is preferable that the alkali or the catalyst can be dissolved in a solvent used for a reaction. Example of the method for mixing the alkali or the catalyst, include a method of adding a solution of alkali or a catalyst slowly, to the reaction solution with stirring under an inert atmosphere of argon, nitrogen, etc. or conversely, a method of adding the reaction solution to the solution of alkali or a catalyst slowly.

[0113]

When these polymeric light-emitting substances of the present invention are used for a light-emitting materials of a polymer LED, the purity thereof exerts an influence on light emitting property, therefore, it is preferable that a monomer is purified by a method such as distillation, sublimation purification, re-crystallization and the like before being polymerized. Further, it is preferable to conduct a purification treatment such as re-precipitation purification, chromatographic separation and the like after the polymerization.

[0114]

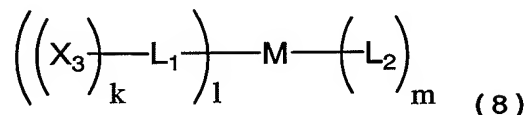
The polymeric light-emitting substance of the present invention can be manufactured by carrying out condensation polymerization of two or more monomers containing monomers represented by the below formulas (7) and (8).



(In the formula, Ar_7 represents an arylene group or a divalent heterocyclic group. R_{17} and R_{18} each independently represent a hydrogen atom, alkyl group, aryl group, a monovalent heterocyclic group, or cyano group. Among the substituents R_{17} and R_{18} on Ar_7 , at least one of them has a substituent represented by the above formula (2) or (3). X_1 and X_2 each independently represent a halogen atom, sulfone oxy group, boric-acid group, the boric ester group, sulfonium methyl group, phosphonium

methyl group, phosphonate methyl group, monohalogenated methyl group, formyl group, cyano group, or vinyl group. n is 0 or 1.)

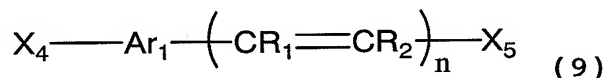
[0115]



(In the formula, M is a metal which is an atom having an atomic number of 50 or more, and intersystem crossing between a singlet state and a triplet state can occur in this complex by spin-orbit interaction. L₁ and L₂ represent ligands which connect to M or more with one or more of a nitrogen atom, an oxygen atom, a carbon atom, a sulfur atom, or a phosphorus atom. X₃ represents a halogen atom, sulfone oxy group, boric-acid group, boric ester group, sulfonium methyl group, phosphonium methyl group, phosphonate methyl group, monohalogenated methyl group, formyl group, cyano group, or vinyl group. k represents an integer of 1-3, l represents an integer of 1-6, and m represents an integer of 0-6.)

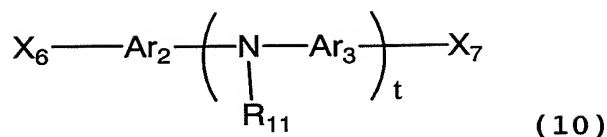
[0116]

Preferably, it can be produced by carrying out condensation polymerization in existence of three or more monomers including the monomers represented by the below formula (9), (10), and the above formula (8).



(In the formula, Ar₁, R₁ and R₂ are the same as those of the above. X₄ and X₅ each independently represent a halogen atom, sulfone oxy group, boric-acid group, boric ester group, sulfonium methyl group, phosphonium methyl group, phosphonate methyl group, monohalogenated methyl group, formyl group, cyano group, or vinyl group. n is 0 or 1.)

[0117]



(In the formula, Ar_2 , Ar_3 , R_{11} and t are the same as those of the above. X_6 and X_7 each independently represent a halogen atom, sulfone oxy group, boric acid group, boric ester group, sulfonium methyl group, phosphonium methyl group, phosphonate methyl group, monohalogenated methyl group, formyl group, cyano group, or vinyl group. However, at least one of R_1 , R_2 , or R_{11} has a substituent shown by the above formula (2) or (3).)

[0118]

As the arylene group or a divalent heterocyclic group in Ar_7 , they are the same as those of the above. As the alkyl group, aryl group and a monovalent heterocyclic group in R_{17} and R_{18} , they are the same with those exemplified as the above R.)

[0119]

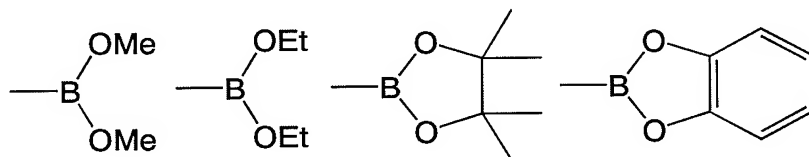
As the halogen atom in X_1 or X_7 , chlorine, bromine, and iodine are exemplified.

[0120]

As the sulfoneoxy group, benzene sulfoneoxy group, p-toluene sulfoneoxy group, methane sulfoneoxy group, ethane sulfoneoxy group, and trifluoromethane sulfoneoxy group are exemplified.

[0121]

As the boric ester group, groups shown by below formulas are exemplified.



[0122]

As the sulfonium methyl group, groups shown by the below formulas are exemplified.

$-CH_2SMe_2X$ and $-CH_2SPh_2X$ (X represents a halogen atom.)

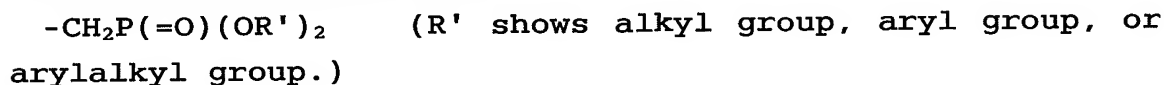
[0123]

As the phosphonium methyl group, groups shown by the below formulas are exemplified.



[0124]

As the phosphonate methyl group, groups shown by the below formulas are exemplified.



[0125]

As the monohalogenated methyl group, chloromethyl group, bromomethyl group, and iodomethyl group are exemplified.

[0126]

As the atom shown by M, rhenium atom, osmium atom, iridium atom, platinum atom, gold atom, lanthanum atom, cerium atom, praseodymium atom, neodymium atom, promethium atom, samarium atom, europium atom, gadolinium atom, terbium atom, dysprosium atom, etc. are exemplified.

Rhenium atom, osmium atom, iridium atom, platinum atom, gold atom, samarium atom, europium atom, gadolinium atom, terbium atom, and dysprosium atom are preferable, and iridium atom, platinum atom, gold atom, and europium atom are more preferable.

[0127]

As the ligand represented by L_1 and L_2 , an alkyl group, alkoxy group, carboxyl group, alkylthio group, alkyl amino group, aryl group, aryloxy group, arylthio group, aryl amino group, arylalkyl group, aryl alkoxy group, aryl alkylthio group, arylalkyl amino group, sulfone oxy group, cyano group, heterocyclic ligand, carbonyl ligand, ether ligand, phosphine ligand, phosphite ligand, and sulfide ligand are exemplified.

[0128]

In the groups represented by L_1 and L_2 , as for the alkyl group, alkoxy group, alkylthio group, alkylamino group, aryl group, aryloxy group, arylthio group, arylamino group, arylalkyl group, arylalkoxy group, arylalkylthio group,

arylalkylamino group, and imino group, the compounds described in the above R are exemplified.

[0129]

In the groups represented by L_1 and L_2 , as for the heterocyclic ligands, exemplified are: ligands consisting of a combination of heterocyclic rings, such as pyridine ring, pyrrole ring, thiophene ring, oxazole and furan ring, and benzene rings; specifically, phenyl pyridine, 2-(para phenyl phenyl)pyridine, 7-bromobenzo[h]quinoline, 2-(4-thiophene-2-yl)pyridine, 2-(4-phenylthiophene-2-yl)pyridine, 2-phenylbenzoxazole, 2-(paraphenylphenyl)benzoxazole, 2-phenylbenzothiazole, 2-(paraphenylphenyl)benzothiazole, 2-(benzothiophene-2-yl)pyridine, 1,10-phenanthroline, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin, etc.

[0130]

The carboxyl group has about 2 to 20 carbon atoms, and specifically, acetyloxy group, trifluoroacetyloxy group, propionyloxy group, and benzoyloxy group are exemplified. As the sulfoneoxy group, benzene sulfoneoxy group, p-toluene sulfoneoxy group, methane sulfoneoxy group, ethane sulfoneoxy group, and trifluoromethane sulfoneoxy group are exemplified.

[0131]

As the carbonyl ligands, exemplified are: carbon monoxide, and acetone; ketones, such as benzophenone; diketones such as, acetyl acetone, and acenaphtho quinine; and diketonates, such as acetylacetonate, dibenzomethylate, and thenoyl trifluoro acetate.

[0132]

As the ether ligands, exemplified are dimethyl ether, diethyl ether, tetrahydrofuran, 1,2-dimethoxy ethane, etc.

[0133]

As the phosphine ligands, exemplified are triphenyl phosphine, diphenylphosphinoethane, and a diphenyl phosphino propane. As the phosphite ligands, exemplified are dimethyl phosphite and diphenyl phosphite.

[0134]

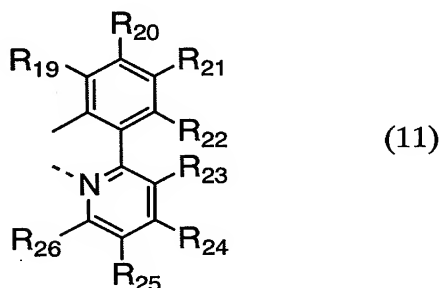
As the sulfide ligand, exemplified are dimethyl sulfide, diphenyl sulfide, and thioanisole.

[0135]

As the ligand represented by L_1 and L_2 , a case where M connect to an at least one carbon atom is preferable, and a case where it is a bidentate ligand which connect to M and forms 5 membered ring is more preferable.

[0136]

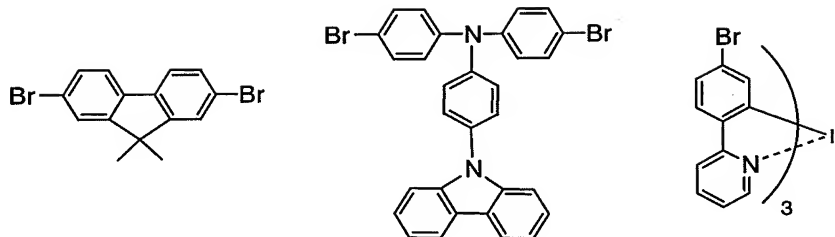
The case shown by the below formula (11) is further preferable.



(In the formula, R_{19} - R_{26} show a hydrogen atom, halogen atom, alkyl group, alkoxy group, alkylthio group, alkyl amino group, alkylsilyl group, aryl group, aryloxy group, arylthio group, arylamino group, arylsilyl group, arylalkyl group, arylalkoxy group, arylalkylthio group, arylalkylamino group, arylalkyl silyl group, acyl group, acyloxy group, imino group, amide group, arylalkenyl group, arylalkynyl group, cyano group, or monovalent heterocyclic group. R_{19} - R_{20} may be connected mutually to form a ring.)

[0137]

The light emitting polymer of the present invention can be manufactured by carrying out condensation polymerization, for example, in existence of a monomer shown below and 0 valent nickel catalyst.



[0138]

Next, the polymer LED of the present invention will be explained. The polymer LED of the present invention comprises an light emitting layer between the electrodes consisting of an anode and a cathode, and the light emitting layer contains the polymeric light-emitting substance of the present invention.

[0139]

As the polymer LED of the present invention, exemplified are: a polymer LED having an electron transporting layer between a cathode and a light emitting layer; a polymer LED having an hole transporting layer between an anode and a light emitting layer; and a polymer LED having an electron transporting layer between an cathode and a light emitting layer, and a hole transporting layer between an anode and a light emitting layer.

Also exemplified are: a polymer LED having a layer containing a conductive polymer between at least one of the electrodes and a light emitting layer adjacently to the electrode; and a polymer LED having a buffer layer having a mean thickness of 2nm or less between at least one of the electrodes and a light emitting layer adjacently to the electrode.

[0140]

The following structures a) to d) are specifically exemplified.

- a) anode/light emitting layer/cathode
- b) anode/hole transporting layer/light emitting layer/cathode
- c) anode/light emitting layer/electron transporting

layer/cathode

d) anode/hole transporting layer/light emitting layer/electron transporting layer/cathode

(wherein, "/" indicates adjacent lamination of layers. Hereinafter, the same).

[0141]

Herein, the light emitting layer is a layer having function to emit a light, the hole transporting layer is a layer having function to transport a hole, and the electron transporting layer is a layer having function to transport an electron. Herein, the electron transporting layer and the hole transporting layer are generically called a charge transporting layer.

The light emitting layer, hole transporting layer and electron transporting layer also may be used each independently in two or more layers.

[0142]

Of charge transporting layers disposed adjacent to an electrode, that having function to improve charge injecting efficiency from the electrode and having effect to decrease driving voltage of an device are particularly called sometimes a charge injecting layer (hole injecting layer, electron injecting layer) in general.

[0143]

For enhancing adherence with an electrode and improving charge injection from an electrode, the above-described charge injecting layer or insulation layer having a thickness of 2 nm or less may also be provided adjacent to an electrode, and further, for enhancing adherence of the interface, preventing mixing and the like, a thin buffer layer may also be inserted into the interface of a charge transporting layer and light emitting layer.

[0144]

The order and number of layers laminated and the thickness of each layer can be appropriately applied while considering light emitting efficiency and life of the device.

[0145]

In the present invention, as the polymer LED having a charge injecting layer (electron injecting layer, hole injecting layer) provided, there are listed a polymer LED having a charge injecting layer provided adjacent to a cathode and a polymer LED having a charge injecting layer provided adjacent to an anode.

[0146]

For example, the following structures e) to p) are specifically exemplified.

e) anode/charge injecting layer/light emitting layer/cathode

f) anode/light emitting layer/charge injecting layer/cathode

g) anode/charge injecting layer/light emitting layer/charge injecting layer/cathode

h) anode/charge injecting layer/hole transporting layer/light emitting layer/cathode

i) anode/hole transporting layer/light emitting layer/charge injecting layer/cathode

j) anode/charge injecting layer/hole transporting layer/light emitting layer/charge injecting layer/cathode

k) anode/charge injecting layer/light emitting layer/electron transporting layer/cathode

l) anode/light emitting layer/electron transporting layer/charge injecting layer/cathode

m) anode/charge injecting layer/light emitting layer/electron transporting layer/charge injecting layer/cathode

n) anode/charge injecting layer/hole transporting layer/light emitting layer/electron transporting layer/cathode

o) anode/hole transporting layer/light emitting layer/electron transporting layer/charge injecting layer/cathode

p) anode/charge injecting layer/hole transporting

layer/light emitting layer/electron transporting
layer/charge injecting layer/cathode

[0147]

As the specific examples of the charge injecting layer, there are exemplified layers containing an conducting polymer, layers which are disposed between an anode and a hole transporting layer and contain a material having an ionization potential between the ionization potential of an anode material and the ionization potential of a hole transporting material contained in the hole transporting layer, layers which are disposed between a cathode and an electron transporting layer and contain a material having an electron affinity between the electron affinity of a cathode material and the electron affinity of an electron transporting material contained in the electron transporting layer, and the like.

[0148]

When the above-described charge injecting layer is a layer containing an conducting polymer, the electric conductivity of the conducting polymer is preferably 10^{-5} S/cm or more and 10^3 S/cm or less, and for decreasing the leak current between light emitting pixels, more preferably 10^{-5} S/cm or more and 10^2 S/cm or less, further preferably 10^{-5} S/cm or more and 10^1 S/cm or less.

[0149]

Usually, to provide an electric conductivity of the conducting polymer of 10^{-5} S/cm or more and 10^3 S/cm or less, a suitable amount of ions are doped into the conducting polymer.

[0150]

Regarding the kind of an ion doped, an anion is used in a hole injecting layer and a cation is used in an electron injecting layer. As examples of the anion, a polystyrene sulfonate ion, alkylbenzene sulfonate ion, camphor sulfonate ion and the like are exemplified, and as examples of the cation, a lithium ion, sodium ion, potassium ion, tetrabutyl ammonium ion and the like are exemplified.

[0151]

The thickness of the charge injecting layer is for example, from 1 nm to 100 nm, preferably from 2 nm to 50 nm.

[0152]

Materials used in the charge injecting layer may properly be selected in view of relation with the materials of electrode and adjacent layers, and there are exemplified conducting polymers such as polyaniline and derivatives thereof, polythiophene and derivatives thereof, polypyrrole and derivatives thereof, poly(phenylene vinylene) and derivatives thereof, poly(thienylene vinylene) and derivatives thereof, polyquinoline and derivatives thereof, polyquinoxaline and derivatives thereof, polymers containing aromatic amine structures in the main chain or the side chain, and the like, and metal phthalocyanine (copper phthalocyanine and the like), carbon and the like.

[0153]

The insulation layer having a thickness of 2 nm or less has function to make charge injection easy. As the material of the above-described insulation layer, metal fluoride, metal oxide, organic insulation materials and the like are listed. As the polymer LED having an insulation layer having a thickness of 2 nm or less, there are listed polymer LEDs having an insulation layer having a thickness of 2 nm or less provided adjacent to a cathode, and polymer LEDs having an insulation layer having a thickness of 2 nm or less provided adjacent to an anode.

[0154]

Specifically, there are listed the following structures q) to ab) for example.

q) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/cathode

r) anode/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

s) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

t) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/cathode

u) anode/hole transporting layer/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

v) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/insulation layer having a thickness of 2 nm or less/cathode

w) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/electron transporting layer/cathode

x) anode/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

y) anode/insulation layer having a thickness of 2 nm or less/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

z) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/electron transporting layer/cathode

aa) anode/hole transporting layer/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

ab) anode/insulation layer having a thickness of 2 nm or less/hole transporting layer/light emitting layer/electron transporting layer/insulation layer having a thickness of 2 nm or less/cathode

[0155]

In producing a polymer LED, when a film is formed from a solution by using such polymeric fluorescent substance soluble in an organic solvent, only required is removal of the solvent by drying after coating of this solution, and even in the case of mixing of a charge transporting material and a light emitting material, the same method can be applied, causing an extreme advantage in production. As the film forming method from a

solution, there can be used coating methods such as a spin coating method, casting method, micro gravure coating method, gravure coating method, bar coating method, roll coating method, wire bar coating method, dip coating method, spray coating method, screen printing method, flexo printing method, offset printing method, inkjet printing method and the like.
[0156]

Regarding the thickness of the light emitting layer, the optimum value differs depending on material used, and may properly be selected so that the driving voltage and the light emitting efficiency become optimum values, and for example, it is from 1 nm to 1 μ m, preferably from 2 nm to 500 nm, further preferably from 5 nm to 200 nm.

[0157]

In the polymer LED of the present invention, light emitting materials other than the above-described polymeric fluorescent substance can also be mixed in a light emitting layer. Further, in the polymer LED of the present invention, the light emitting layer containing light emitting materials other than the above-described polymeric fluorescent substance may also be laminated with a light emitting layer containing the above-described polymeric fluorescent substance.

[0158]

As the light emitting material, known materials can be used. In a compound having lower molecular weight, there can be used, for example, naphthalene derivatives, anthracene or derivatives thereof, perylene or derivatives thereof; dyes such as polymethine dyes, xanthene dyes, coumarine dyes, cyanine dyes; metal complexes of 8-hydroxyquinoline or derivatives thereof, aromatic amine, tetraphenylcyclopentane or derivatives thereof, or tetraphenylbutadiene or derivatives thereof, and the like.

[0159]

Specifically, there can be used known compounds such as those described in JP-A Nos. 57-51781, 59-195393 and the like,

for example.

[0160]

When the polymer LED of the present invention has a hole transporting layer, as the hole transporting materials used, there are exemplified polyvinylcarbazole or derivatives thereof, polysilane or derivatives thereof, polysiloxane derivatives having an aromatic amine in the side chain or the main chain, pyrazoline derivatives, arylamine derivatives, stilbene derivatives, triphenyldiamine derivatives, polyaniline or derivatives thereof, polythiophene or derivatives thereof, polypyrrole or derivatives thereof, poly(p-phenylenevinylene) or derivatives thereof, poly(2,5-thienylenevinylene) or derivatives thereof, or the like.

[0161]

Specific examples of the hole transporting material include those described in JP-A Nos. 63-70257, 63-175860, 2-135359, 2-135361, 2-209988, 3-37992 and 3-152184.

[0162]

Among them, as the hole transporting materials used in the hole transporting layer, preferable are polymer hole transporting materials such as polyvinylcarbazole or derivatives thereof, polysilane or derivatives thereof, polysiloxane derivatives having an aromatic amine compound group in the side chain or the main chain, polyaniline or derivatives thereof, polythiophene or derivatives thereof, poly(p-phenylenevinylene) or derivatives thereof, poly(2,5-thienylenevinylene) or derivatives thereof, or the like, and further preferable are polyvinylcarbazole or derivatives thereof, polysilane or derivatives thereof and polysiloxane derivatives having an aromatic amine compound group in the side chain or the main chain. In the case of a hole transporting material having lower molecular weight, it is preferably dispersed in a polymer binder for use.

[0163]

Polyvinylcarbazole or derivatives thereof are obtained,

for example, by cation polymerization or radical polymerization from a vinyl monomer.

[0164]

As the polysilane or derivatives thereof, there are exemplified compounds described in Chem. Rev., 89, 1359 (1989) and GB 2300196 published specification, and the like. For synthesis, methods described in them can be used, and a Kipping method can be suitably used particularly.

[0165]

As the polysiloxane or derivatives thereof, those having the structure of the above-described hole transporting material having lower molecular weight in the side chain or main chain, since the siloxane skeleton structure has poor hole transporting property. Particularly, there are exemplified those having an aromatic amine having hole transporting property in the side chain or main chain.

[0166]

The method for forming a hole transporting layer is not restricted, and in the case of a hole transporting layer having lower molecular weight, a method in which the layer is formed from a mixed solution with a polymer binder is exemplified. In the case of a polymer hole transporting material, a method in which the layer is formed from a solution is exemplified.

[0167]

The solvent used for the film forming from a solution is not particularly restricted providing it can dissolve a hole transporting material. As the solvent, there are exemplified chlorine solvents such as chloroform, methylene chloride, dichloroethane and the like, ether solvents such as tetrahydrofuran and the like, aromatic hydrocarbon solvents such as toluene, xylene and the like, ketone solvents such as acetone, methyl ethyl ketone and the like, and ester solvents such as ethyl acetate, butyl acetate, ethylcellosolve acetate and the like.

[0168]

As the film forming method from a solution, there can be

used coating methods such as a spin coating method, casting method, micro gravure coating method, gravure coating method, bar coating method, roll coating method, wire bar coating method, dip coating method, spray coating method, screen printing method, flexo printing method, offset printing method, inkjet printing method and the like, from a solution.

[0169]

The polymer binder mixed is preferably that does not disturb charge transport extremely, and that does not have strong absorption of a visible light is suitably used. As such polymer binder, polycarbonate, polyacrylate, poly(methyl acrylate), poly(methyl methacrylate), polystyrene, poly(vinyl chloride), polysiloxane and the like are exemplified.

[0170]

Regarding the thickness of the hole transporting layer, the optimum value differs depending on material used, and may properly be selected so that the driving voltage and the light emitting efficiency become optimum values, and at least a thickness at which no pin hole is produced is necessary, and too large thickness is not preferable since the driving voltage of the device increases. Therefore, the thickness of the hole transporting layer is, for example, from 1 nm to 1 μ m, preferably from 2 nm to 500 nm, further preferably from 5 nm to 200 nm.

[0171]

When the polymer LED of the present invention has an electron transporting layer, known compounds are used as the electron transporting materials, and there are exemplified oxadiazole derivatives, anthraquinonedimethane or derivatives thereof, benzoquinone or derivatives thereof, naphthoquinone or derivatives thereof, anthraquinone or derivatives thereof, tetracyanoanthraquinodimethane or derivatives thereof, fluorenone derivatives, diphenyldicyanoethylene or derivatives thereof, diphenoquinone derivatives, or metal complexes of

8-hydroxyquinoline or derivatives thereof, polyquinoline and derivatives thereof, polyquinoxaline and derivatives thereof, polyfluorene or derivatives thereof, and the like.

[0172]

Specifically, there are exemplified those described in JP-A Nos. 63-70257, 63-175860, 2-135359, 2-135361, 2-209988, 3-37992 and 3-152184.

[0173]

Among them, oxadiazole derivatives, benzoquinone or derivatives thereof, anthraquinone or derivatives thereof, or metal complexes of 8-hydroxyquinoline or derivatives thereof, polyquinoline and derivatives thereof, polyquinoxaline and derivatives thereof, polyfluorene or derivatives thereof are preferable, and 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole, benzoquinone, anthraquinone, tris(8-quinolinol)aluminum and polyquinoline are further preferable.

[0174]

The method for forming the electron transporting layer is not particularly restricted, and in the case of an electron transporting material having lower molecular weight, a vapor deposition method from a powder, or a method of film-forming from a solution or melted state is exemplified, and in the case of a polymer electron transporting material, a method of film-forming from a solution or melted state is exemplified, respectively.

[0175]

The solvent used in the film-forming from a solution is not particularly restricted provided it can dissolve electron transporting materials and/or polymer binders. As the solvent, there are exemplified chlorine solvents such as chloroform, methylene chloride, dichloroethane and the like, ether solvents such as tetrahydrofuran and the like, aromatic hydrocarbon solvents such as toluene, xylene and the like, ketone solvents such as acetone, methyl ethyl ketone and the like, and ester solvents such as ethyl acetate, butyl acetate,

ethylcellosolve acetate and the like.

[0176]

As the film-forming method from a solution or melted state, there can be used coating methods such as a spin coating method, casting method, micro gravure coating method, gravure coating method, bar coating method, roll coating method, wire bar coating method, dip coating method, spray coating method, screen printing method, flexo printing method, offset printing method, inkjet printing method and the like.

[0177]

The polymer binder to be mixed is preferably that which does not extremely disturb a charge transport property, and that does not have strong absorption of a visible light is suitably used. As such polymer binder, poly(N-vinylcarbazole), polyaniline or derivatives thereof, polythiophene or derivatives thereof, poly(p-phenylene vinylene) or derivatives thereof, poly(2,5-thienylene vinylene) or derivatives thereof, polycarbonate, polyacrylate, poly(methyl acrylate), poly(methyl methacrylate), polystyrene, poly(vinyl chloride), polysiloxane and the like are exemplified.

[0178]

Regarding the thickness of the electron transporting layer, the optimum value differs depending on material used, and may properly be selected so that the driving voltage and the light emitting efficiency become optimum values, and at least a thickness at which no pin hole is produced is necessary, and too large thickness is not preferable since the driving voltage of the device increases. Therefore, the thickness of the electron transporting layer is, for example, from 1 nm to 1 μ m, preferably from 2 nm to 500 nm, further preferably from 5 nm to 200 nm.

[0179]

The substrate forming the polymer LED of the present invention may preferably be that does not change in forming an electrode and layers of organic materials, and there are

exemplified glass, plastics, polymer film, silicon substrates and the like. In the case of a opaque substrate, it is preferable that the opposite electrode is transparent or semitransparent.

[0180]

Usually, at least one of the electrodes consisting of an anode and a cathode, is transparent or semitransparent. It is preferable that the anode is transparent or semitransparent.

As the material of this anode, electron conductive metal oxide films, semitransparent metal thin films and the like are used. Specifically, there are used indium oxide, zinc oxide, tin oxide, and films (NESA and the like) fabricated by using an electron conductive glass composed of indium/tin/oxide (ITO), indium/zinc/oxide and the like, which are metal oxide complexes, and gold, platinum, silver, copper and the like are used, and among them, ITO, indium/zinc/oxide, tin oxide are preferable. As the fabricating method, a vacuum vapor deposition method, sputtering method, ion plating method, plating method and the like are used. As the anode, there may also be used organic transparent conducting films such as polyaniline or derivatives thereof, polythiophene or derivatives thereof and the like.

[0181]

The thickness of the anode can be appropriately selected while considering transmission of a light and electric conductivity, and for example, from 10 nm to 10 μ m, preferably from 20 nm to 1 μ m, further preferably from 50 nm to 500 nm.

[0182]

Further, for easy charge injection, there may be provided on the anode a layer comprising a phthalocyanine derivative conducting polymers, carbon and the like, or a layer having an average film thickness of 2 nm or less comprising a metal oxide, metal fluoride, organic insulating material and the like.

[0183]

As the material of a cathode used in the polymer LED of

the present invention, that having lower work function is preferable. For example, there are used metals such as lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, aluminum, scandium, vanadium, zinc, yttrium, indium, cerium, samarium, europium, terbium, ytterbium and the like, or alloys comprising two of more of them, or alloys comprising one or more of them with one or more of gold, silver, platinum, copper, manganese, titanium, cobalt, nickel, tungsten and tin, graphite or graphite intercalation compounds and the like. Examples of alloys include a magnesium-silver alloy, magnesium-indium alloy, magnesium-aluminum alloy, indium-silver alloy, lithium-aluminum alloy, lithium-magnesium alloy, lithium-indium alloy, calcium-aluminum alloy and the like. The cathode may be formed into a laminated structure of two or more layers.

[0184]

The thickness of the cathode can be appropriately selected while considering transmission of a light and electric conductivity, and for example, from 10 nm to 10 μ m, preferably from 20 nm to 1 μ m, further preferably from 50 nm to 500 nm.

[0185]

As the method for fabricating a cathode, there are used a vacuum vapor deposition method, sputtering method, lamination method in which a metal thin film is adhered under heat and pressure, and the like. Further, there may also be provided, between a cathode and an organic layer, a layer comprising an conducting polymer, or a layer having an average film thickness of 2 nm or less comprising a metal oxide, metal fluoride, organic insulation material and the like, and after fabrication of the cathode, a protective layer may also be provided which protects the polymer LED. For stable use of the polymer LED for a long period of time, it is preferable to provide a protective layer and/or protective cover for protection of the device in order to prevent it from outside

damage.

[0186]

As the protective layer, there can be used a polymeric compound, metal oxide, metal fluoride, metal borate and the like. As the protective cover, there can be used a glass plate, a plastic plate the surface of which has been subjected to lower-water-permeation treatment, and the like, and there is suitably used a method in which the cover is pasted with an device substrate by a thermosetting resin or light-curing resin for sealing. If space is maintained using a spacer, it is easy to prevent an device from being injured. If an inner gas such as nitrogen and argon is sealed in this space, it is possible to prevent oxidation of a cathode, and further, by placing a desiccant such as barium oxide and the like in the above-described space, it is easy to suppress the damage of an device by moisture adhered in the production process. Among them, any one means or more are preferably adopted.

[0187]

The polymer LED of the present invention can be used for a flat light source, a segment display, a dot matrix display, and a liquid crystal display as a back light, etc.

For obtaining light emission in plane form using the polymer LED of the present invention, an anode and a cathode in the plane form may properly be placed so that they are laminated each other. Further, for obtaining light emission in pattern form, there is a method in which a mask with a window in pattern form is placed on the above-described plane light emitting device, a method in which an organic layer in non-light emission part is formed to obtain extremely large thickness providing substantial non-light emission, and a method in which any one of an anode or a cathode, or both of them are formed in the pattern. By forming a pattern by any of these methods and by placing some electrodes so that independent on/off is possible, there is obtained a display device of segment type which can display digits, letters, simple marks and the like. Further, for forming a dot matrix device, it

may be advantageous that anodes and cathodes are made in the form of stripes and placed so that they cross at right angles. By a method in which a plurality of kinds of polymeric compounds emitting different colors of lights are placed separately or a method in which a color filter or luminescence converting filter is used, area color displays and multi color displays are obtained. A dot matrix display can be driven by passive driving, or by active driving combined with TFT and the like. These display devices can be used as a display of a computer, television, portable terminal, portable telephone, car navigation, view finder of a video camera, and the like.

[0188]

Further, the above-described light emitting device in plane form is a thin self-light-emitting one, and can be suitably used as a flat light source for back-light of a liquid crystal display, or as a flat light source for illumination. Further, if a flexible plate is used, it can also be used as a curved light source or a display.

[0189]

[Effect of the Invention]

The polymeric light-emitting substance of the present invention has triplet light-emitting complex structure in a molecule, and can form a light emitting layer by industrially simple application methods, such as a spin coat method, an ink-jet method, and a printing method. Moreover, the polymeric light-emitting substance of the present invention contains triplet light-emitting complex, and can show high light emitting efficiency. Therefore, the polymeric light-emitting substance of the present invention can be used preferably for light-emitting materials of polymer LED etc.

[Name of Document] ABSTRACT

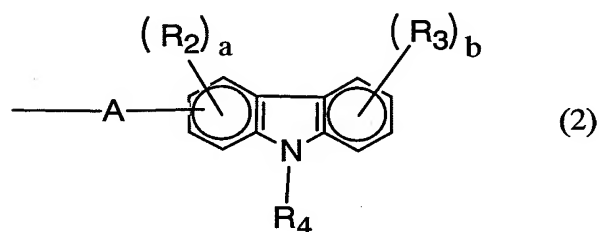
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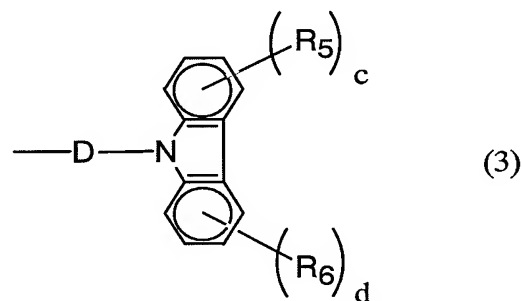
To provide a new polymeric light emitting substance having a triplet light emitting metal complex structure in the molecule, which can form a light emitting layer by coating method.

[Solving Means]

A polymeric light emitting substance having a triplet light emitting complex structure in the main chain or side chain, and a mono-valent group represented by the following formula (2) or (3),



(in the formula, A is a conjugated divalent group. R_2 and R_3 represent a halogen atom, alkyl group, alkoxy group, etc. R_4 represents an alkyl group, aryl group, etc. a represents an integer of 0 to 3. b represents an integer of 0 to 4.)



(in the formula, D is a conjugated divalent group. R_5 and R_6 represent a halogen atom, alkyl group, alkoxy group, etc. c and d each independently represent an integer of 0 to 4.)

[Selected Figure] No